

A First Course on Kinetics and Reaction Engineering

Example 35.1

Problem Statement

A tube that is 6 m long with an inside diameter of 7 cm is packed with pellets of solid catalyst. Reaction (1) takes place within this reactor at a constant temperature of 450 °C and a constant pressure of 5 atm. The tube will be fed 200 ft³ h⁻¹ of a gas containing 15% A, 15% B and 70% I (an inert gas). Reaction (1) is one-half order in A and first order in B. Suppose that the packing in the tube is not uniform, and as a consequence 5% of the bed has a lower density (leading to a rate coefficient of 59.5 mol h⁻¹ atm^{-0.5} m⁻³), while the remainder has a higher density (with a rate coefficient of 72 mol h⁻¹ atm^{-0.5} m⁻³). Using a zoned reactor model with two parallel PFR zones, show how the conversion will vary as the fraction of the feed gas flowing into the less dense part of the bed varies between 0 and 25%.



Problem Analysis

The problem statement tells us what reaction is taking place, and we are given the rate expression for it. We are provided with quantitative reactor specifications, and we are asked to calculate a reactor performance metric, namely the conversion. Thus, this is a quantitative reaction engineering problem, but in addition, it involves a zoned reactor model. In this particular problem the zoned reactor model consists of two PFRs connected in parallel, making this a reactor network problem.

Problem Solution

The reactor network described in the problem statement is sketched in Figure 1 where the two PFRs are labeled as R1 and R2, the stream split is labeled as SS1, the stream merge is labeled as SM1 and the six flow streams are labeled as FS1 through FS6. Here we will let R2 represent the PFR with the lower packing density.

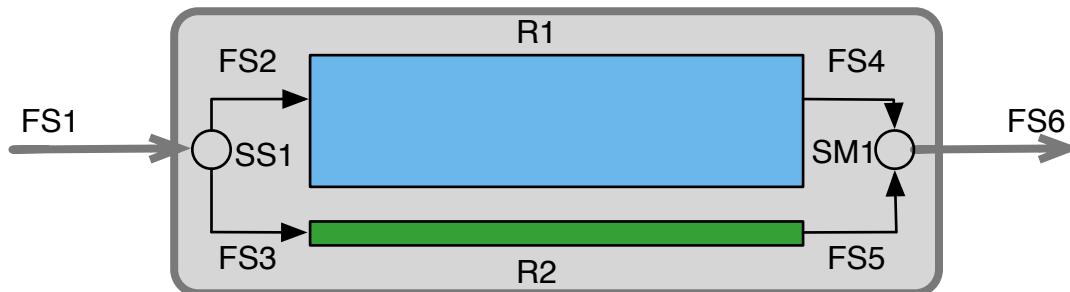


Figure 1. Schematic representation of the zoned reactor model indicating labels for flow streams (FS), reactors (R), stream splits (SS) and stream merges (SM).

In terms of the labeling in Figure 1, the problem statement provides values for the following quantities: $L_{actual} = 6\text{m}$, $D_{actual} = 7\text{ cm}$, $T = 450\text{ }^\circ\text{C}$, $P = 5\text{ atm}$, $\dot{V}_{FS1} = 200\text{ ft}^3\text{ h}^{-1}$, $y_{A,FS1} = 0.15$, $y_{B,FS1} = 0.15$, $y_{I,FS1} = 0.7$, $k_{1,R2} = 59.5\text{ mol h}^{-1}\text{ atm}^{-0.5}\text{ m}^{-3}$ and $k_{1,R1} = 72\text{ mol h}^{-1}\text{ atm}^{-0.5}\text{ m}^{-3}$, where the subscript “actual” denotes the actual reactor that is being modeled as the network of Figure 1. The problem statement also provides the rate expression, equation (2) and the ratio of the PFR volumes, equation (3). We are asked to plot the conversion of A, f_A , versus q_{R2} (the percentage of \dot{V}_{FS1} that splits off to become flow stream FS3) over the range from 0 to 25%.

$$r_1 = k_1 C_A^{0.5} C_B \quad (2)$$

$$V_{R2} = 0.05 V_{actual} \quad (3)$$

The reactor design equations can now be written for each of the two reactors. The problem statement specifies that the temperature is constant within the reactors, so the mole balance design equations can be solved independently of the energy balance equations. Furthermore, since the problem does not ask anything about heat transfer, the energy balance equation will not be needed in order to answer the questions posed in this problem. The general form of the PFR mole balance design equation is given in equation (4). In this problem, the reactors operate at steady state, so the time derivatives are equal to zero and the derivative with respect to z is an ordinary derivative. There is only one reaction, so the summation in equation (4) reduces to a single term. Thus, applying this equation to A, B and Z in each of the two reactors leads to equations (5) through (10).

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all \\ \text{reactions}}} v_{i,j} r_j - \frac{\pi D^2}{4\dot{V}} \frac{\partial \dot{n}_i}{\partial t} + \frac{\pi D^2 \dot{n}_i}{4\dot{V}^2} \frac{\partial \dot{V}}{\partial t} \quad (4)$$

$$\frac{d\dot{n}_{A,R1}}{dz} = -2 \frac{\pi D_{R1}^2}{4} r_{1,R1}; \quad \dot{n}_{A,R1}(0) = \dot{n}_{A,FS2} \quad (5)$$

$$\frac{d\dot{n}_{B,R1}}{dz} = -\frac{\pi D_{R1}^2}{4} r_{1,R1}; \quad \dot{n}_{B,R1}(0) = \dot{n}_{B,FS2} \quad (6)$$

$$\frac{d\dot{n}_{Z,R1}}{dz} = 2 \frac{\pi D_{R1}^2}{4} r_{1,R1}; \quad \dot{n}_{Z,R1}(0) = \dot{n}_{Z,FS2} \quad (7)$$

$$\frac{d\dot{n}_{A,R2}}{dz} = -2 \frac{\pi D_{R2}^2}{4} r_{1,R2}; \quad \dot{n}_{A,R2}(0) = \dot{n}_{A,FS3} \quad (8)$$

$$\frac{d\dot{n}_{B,R2}}{dz} = -\frac{\pi D_{R2}^2}{4} r_{1,R2}; \quad \dot{n}_{B,R2}(0) = \dot{n}_{B,FS3} \quad (9)$$

$$\frac{d\dot{n}_{Z,R2}}{dz} = 2 \frac{\pi D_{R2}^2}{4} r_{1,R2}; \quad \dot{n}_{Z,R2}(0) = \dot{n}_{Z,FS3} \quad (10)$$

At this point, none of these equations can be solved because the necessary initial conditions are not given. They can be calculated using mole balances at stream split SS1. Recall that we will be making a plot of the conversion as a function of the percentage of the feed flow that passes through the less dense part of the bed, which here corresponds to reactor R2. For a given fraction of the flow passing through reactor R2, q_{R2} , the total molar flow entering reactors R1 and R2 can be calculated using the ideal gas law, as shown in equations (11) and (12).

$$\dot{n}_{tot,FS3} = \frac{q_{R2} \dot{V}_{FS1} P}{RT} \quad (11)$$

$$\dot{n}_{tot,FS2} = \frac{(1 - q_{R2}) \dot{V}_{FS1} P}{RT} \quad (12)$$

The mole fractions of the species are not changed upon splitting flow stream FS1; the mole fractions in FS2 and FS3 are the same as in FS1. Thus, the molar flow rates of A, B and Z in flow streams FS2 and FS3 can be calculated using equations (13) through (18).

$$\dot{n}_{A,FS2} = y_{A,FS1} \dot{n}_{tot,FS2} \quad (13)$$

$$\dot{n}_{B,FS2} = y_{B,FS1} \dot{n}_{tot,FS2} \quad (14)$$

$$\dot{n}_{Z,FS2} = y_{Z,FS1} \dot{n}_{tot,FS2} \quad (15)$$

$$\dot{n}_{A,FS3} = y_{A,FS1} \dot{n}_{tot,FS3} \quad (16)$$

$$\dot{n}_{B,FS3} = y_{B,FS1} \dot{n}_{tot,FS3} \quad (17)$$

$$\dot{n}_{Z,FS3} = y_{Z,FS1} \dot{n}_{tot,FS3} \quad (18)$$

It still isn't possible to solve any of the mole balance design equations, however, because the length and diameter of the two PFRs in the zoned reactor model were not specified. However, the volumes of the two PFR zones can be computed, equations (19), (3) and (20), and the design equations can be rewritten to use the reactor zone volumes as the dependent variables. This is illustrated for equation (5) in equation (21); the other mole balances can be similarly modified.

$$V_{actual} = \frac{\pi D_{actual}^2 L_{actual}}{4} \quad (19)$$

$$V_{R1} = V_{actual} - V_{R2} \quad (20)$$

$$\frac{d\dot{n}_{A,R1}}{dz} = -2 \frac{\pi D_{R1}^2}{4} r_{1,R1} \Rightarrow \frac{d\dot{n}_{A,R1}}{d\left(\frac{\pi D_{R1}^2}{4} z\right)} = -2 r_{1,R1} \Rightarrow \frac{d\dot{n}_{A,R1}}{dV} = -2 r_{1,R1} \quad (21)$$

At this point, the design equations for reactor R1 can be solved numerically, as can the design equations for reactor R2. In order to do so, for each set of design equations it will be necessary to provide initial conditions, one final condition and code that evaluates the right-hand sides of the design equations given values for the independent and dependent variables. The initial conditions at $V = 0$ are specified in equations (5) through (10), and their values can be computed as indicated in equations (13) through (18). The final conditions are $V = V_{R1}$ and V_{R2} , respectively. The code that evaluates the right-hand sides of the design equations will be given values for the independent (V) and dependent ($\dot{n}_{A,R1}$, $\dot{n}_{B,R1}$ and $\dot{n}_{Z,R1}$ or $\dot{n}_{A,R2}$, $\dot{n}_{B,R2}$ and $\dot{n}_{Z,R2}$, respectively) variables. Looking at equations (5) through (10) and recognizing that they will be re-written as indicated in equation (21), the only unknown quantities that appear on the right-hand sides of the mole balances are the rates. These can be calculated using equations (22) and (23). In order to do so, the concentrations of A and B must first be computed. These are found using the definition of concentration and the ideal gas law, as shown in equations (24) through (27).

$$r_{1,R1} = k_{1,R1} C_{A,R1}^{0.5} C_{B,R1} \quad (22)$$

$$r_{1,R2} = k_{1,R2} C_{A,R2}^{0.5} C_{B,R2} \quad (23)$$

$$C_{A,Rj} = \frac{\dot{n}_{A,Rj}}{\dot{V}_{Rj}}; \quad C_{B,Rj} = \frac{\dot{n}_{B,Rj}}{\dot{V}_{Rj}} \quad (24)$$

$$\dot{V}_{Rj} = \frac{(\dot{n}_{A,Rj} + \dot{n}_{B,Rj} + \dot{n}_{Z,Rj} + \dot{n}_{I,Rj}) RT}{P} \quad (25)$$

$$\dot{n}_{I,R1} = \dot{n}_{I,FS2} = y_{I,FS1} \dot{n}_{tot,FS2} \quad (26)$$

$$\dot{n}_{I,R2} = \dot{n}_{I,FS3} = y_{I,FS1} \dot{n}_{tot,FS3} \quad (27)$$

At this point, a value for q_{R2} can be chosen, and the design equations for reactors R1 and R2 can be solved numerically. This will yield the outlet flow rates of A, B and Z in streams FS4 and FS5. The conversion can then be computed using equation (28), where a mole balance on stream merge SM1 has been used to find the molar flow rate of A in flow stream FS6, and then the overall conversion has been computed in terms of the flow of A in flow streams FS1 and FS6. The entire solution procedure can be repeated for a number of values of q_{R1} , and the results can be plotted, leading to Figure 2.

$$f_A = \frac{\dot{n}_{A,FS1} - (\dot{n}_{A,FS4} + \dot{n}_{A,FS5})}{\dot{n}_{A,FS1}} \quad (28)$$

The maximum seen in Figure 2 is consistent with the discussion presented in Unit 29. Specifically, Unit 29 cautioned that "if parallel reactors are used, one should avoid mixing streams of unequal conversion; this effectively undoes some of the reaction that has taken place because after mixing the effective conversion of the mixed stream will be lower than that in the stream with the higher conversion

before mixing.” The maximum in Figure 2 corresponds to the situation where the conversions in the two zones are equal; on either side of the maximum, the conversion in the two zones are unequal.

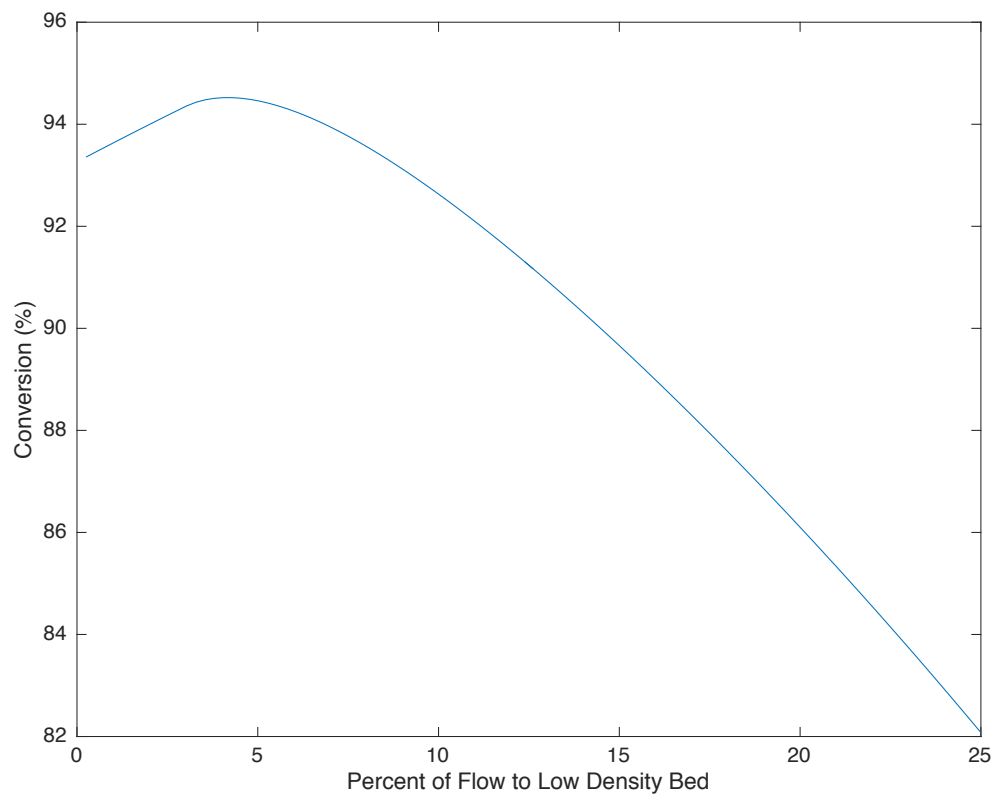


Figure 2. Variation in the conversion as a function of the percentage of the feed that flows through the less dense part of the packed bed.

Calculation Details Using MATLAB

The design equations for the two PFR zones are identical; they differ in the value of the rate coefficient, the inlet molar flow rates and in the reactor zone volume. As such, I decided to write one MATLAB function that could solve the design equations for either PFR zone. That function was written by modification of the MATLAB template file SolvIVDifl.m. The first necessary modification was to change the function so it receives two arguments and returns a single vector. The first argument is a string which is used to identify which reactor to model; this string is named `reactor` and its value will either be 'R1' or 'R2'. The second argument, named `q_R2`, is the fraction of the total inlet flow that enters reaction zone R2. The vector that the function returns is named `z` and it contains the outlet molar flow rates of A, B and Z. The second necessary modification was to enter all of the known constants that were given in the problem specification or that could be calculated from the given quantities. All of these modifications can be seen in Listing 1.

```

function z = Example_35_1_PFR(reactor,q_R2)
% Known quantities and constants
L_actual = 6; % m
D_actual = 7 / 100; % m
T = 450 + 273.15; % K
P = 5; % atm
VFR_FS1 = 200 * 0.02832; % m^3/h
yA_FS1 = 0.15;
yB_FS1 = 0.15;
yI_FS1 = 0.7;
yZ_FS1 = 0.0;
k1_R1 = 72; % mol/(h m^3 atm^0.5)
k1_R2 = 59.5; % mol/(h m^3 atm^0.5)
% Universal Constants
Rpv = 0.08206E-3; % m3 atm/(mol K)
% Additional Calculated Constants
ntot_FS1 = P*VFR_FS1/Rpv/T; % mol/h, ideal gas law
nA_FS1 = yA_FS1*ntot_FS1; % mol/h
nB_FS1 = yB_FS1*ntot_FS1; % mol/h
nZ_FS1 = yZ_FS1*ntot_FS1; % mol/h
nI_FS1 = yI_FS1*ntot_FS1; % mol/h
V_actual = pi()*D_actual^2*L_actual/4; % m3
V_R2 = 0.05*V_actual; % m3
V_R1 = 0.95*V_actual; % m3

```

Listing 1. Modifications involving the function name, function arguments, function return value and constants.

The second modification involved checking the value of the reactor variable to determine which reactor was being modeled, and then setting the rate coefficient, reactor zone volume and molar flow rates to the appropriate values. These modifications can be seen in Listing 2. Note that the final condition is the reactor zone volume, so t_f was set equal to the appropriate volume. Similarly, the initial conditions are the molar flow rates of A, B and Z, so the elements of the vector z_0 were set equal to the corresponding values.

The third modification occurred within the internal function `odeqns`, and it involved adding the code to evaluate the right hand side of the three design equations. When I ran the code, I encountered problems associated with the square root of the concentration of A that appears in the rate expression. Because the numerical solution algorithm may use a step change in z that results in C_A being negative, this introduced imaginary numbers. Therefore, I added a statement to simply set the rate equal to zero whenever the concentration of A was zero or less. All of these modifications can be seen in Listing 3.

No further modifications were required. The resulting function `Example_35_1_PFR.m` accompanies this solution. A second MATLAB function was written to model the reactor network using a range of values for q_{R2} , and plot the results. That function is quite straightforward and accompanies this solution. The file is named `Example_35_1`. It calls `Example_35_1_PFR` to perform the reactor zone modeling; running it generates Figure 2.

```

% Set constants, initial conditions and final condition for the
% reactor
if (reactor == 'R1')
    k1 = k1_R1;
    tf = V_R1;
    ntot_FS2 = (1-q_R2)*ntot_FS1;
    nI = yI_FS1*ntot_FS2;
    z0 = [
        yA_FS1*ntot_FS2;
        yB_FS1*ntot_FS2;
        yZ_FS1*ntot_FS2;
    ];
elseif (reactor == 'R2')
    k1 = k1_R2;
    tf = V_R2;
    ntot_FS3 = (q_R2)*ntot_FS1;
    nI = yI_FS1*ntot_FS3;
    z0 = [
        yA_FS1*ntot_FS3;
        yB_FS1*ntot_FS3;
        yZ_FS1*ntot_FS3;
    ];
else
    display(['Unknown Reactor: ' reactor])
end

```

Listing 2. Code that sets the rate coefficient, reactor zone volume and initial molar flows according to which reactor is being modeled.

```

% Function that evaluates the ODEs
function dzdt = odeqns(t,z)
    nA = z(1);
    nB = z(2);
    nZ = z(3);
    CA = nA*P/((nA + nB + nZ + nI)*Rpv*T);
    CB = nB*P/((nA + nB + nZ + nI)*Rpv*T);
    r = k1*sqrt(CA)*CB;
    if (CA <= 0.0)
        r = 0.0;
    end
    dzdt = [
        -2*r;
        -r;
        2*r;
    ];
end % of internal function odeqns

```

Listing 3. Code that evaluates the ODEs being solved.