

A First Course on Kinetics and Reaction Engineering

Example 35.2

Problem Statement

Irreversible, liquid phase reactions (1) and (2) take place in an isothermal CSTR. The rate expressions are given in equations (3) and (4). At the process temperature the rate coefficients, k_1 and k_2 equal $0.0017 \text{ L mol}^{-1} \text{ s}^{-1}$ and $0.021 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively. The reactor holds 500 L of solution, and is fed 75 L min^{-1} of a solution containing A and B at concentrations of 2.9 mol L^{-1} and 3.2 mol L^{-1} , respectively. It is suspected that some small fraction of the liquid volume is not being well mixed with the remainder of the liquid, and consequently the ideal CSTR model does not accurately predict the reactor's performance. Formulate a zoned reactor model wherein 15% of the fluid volume is a well-mixed stagnant zone that exchanges fluid with the remainder of the reactor volume at a rate of 1 L min^{-1} . According to the resulting zoned reactor model, what will the conversion of A equal and what will the ratio of S to Z equal?



$$r_1 = k_1 C_A C_B \quad (3)$$

$$r_2 = k_2 C_R C_B \quad (4)$$

Problem Analysis

The problem statement tells us what reactions are taking place, and we are given the rate expression for them. We are provided with quantitative reactor specifications, and we are asked to calculate a reactor performance metric, namely the time necessary to reach a specified conversion. Thus, this is a quantitative reaction engineering problem, but in addition, it involves a zoned reactor model, making it a reactor network problem. In this particular problem the zoned reactor model consists of a main zone and a perfectly mixed stagnant zone. There is flow between the two zones, making them both CSTRs.

Problem Solution

The reactor network described in the problem statement is sketched in Figure 1 where the two CSTR zones are labeled as R1 and R2. Here we will let R1 represent the main zone and R2 will represent the well-mixed stagnant zone. The four flow streams also are labeled as FS1, FS2, FS3 and FS4. Using that labeling and assuming constant density, the following quantities are given in the problem statement: $k_1 = 0.0017 \text{ L mol}^{-1} \text{ s}^{-1}$, $k_2 = 0.021 \text{ L mol}^{-1} \text{ s}^{-1}$, $V_{tot} = 500 \text{ L}$, $\dot{V}_{FS1} = \dot{V}_{FS2} = 75 \text{ L min}^{-1}$, $\dot{V}_{FS3} = \dot{V}_{FS4} = 1 \text{ L min}^{-1}$, $C_{A,1} = 2.9 \text{ mol L}^{-1}$, $C_{B,1} = 3.2 \text{ mol L}^{-1}$ and $V_{R2} = 0.15 V_{tot}$. We are asked to compute f_A and $S_{S/Z}$.

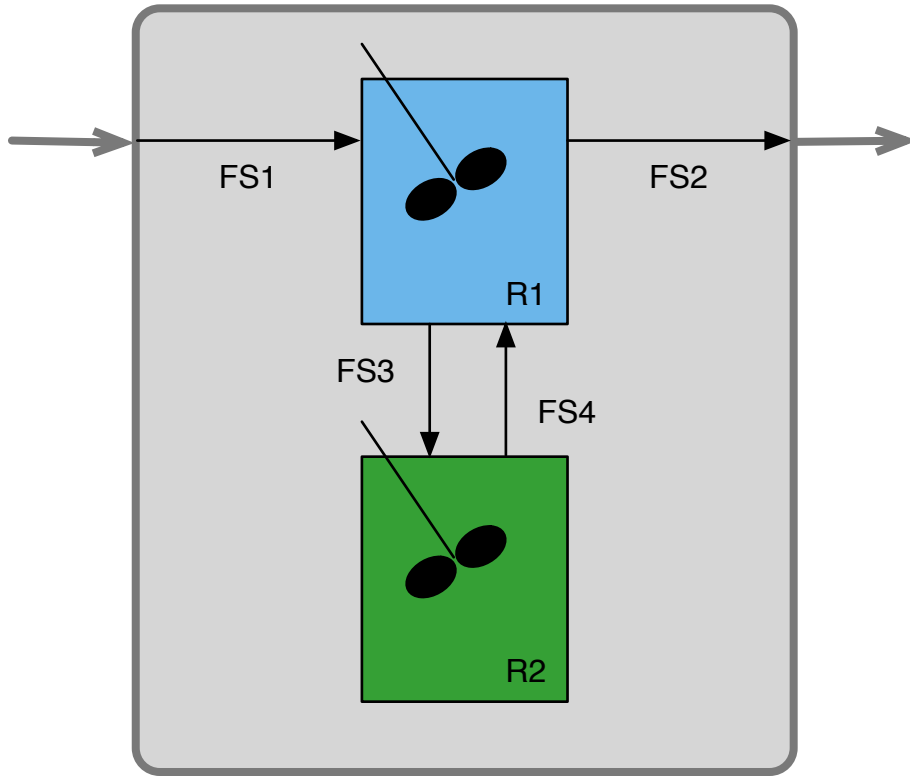


Figure 1. Schematic representation of the zoned reactor model indicating labels for flow streams (FS), and reactors (R).

Since the reactor is isothermal, the mole balance design equations can be solved independently of the energy balance design equations. In this problem the energy balance design equations will not be needed to calculate the requested quantities. The general form of the steady state CSTR mole balance design equation is given in equation (5). For reactor R1, the molar flow into the reactor will be the sum of the molar flows in flow streams FS1 and FS4, and the molar outflow will be the sum of the molar flows in flow streams FS2 and FS3. In both cases, the summation will expand to two terms since there are two reactions taking place. Applying these simplifications, mole balances on A, B, R, S, Y and Z can be written for each of the two CSTR zones, R1 and R2.

$$\dot{n}_i^0 - \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} \nu_{i,j} r_j = 0 \quad (5)$$

$$\dot{n}_{A,FS1} + \dot{n}_{A,FS4} - \dot{n}_{A,FS2} - \dot{n}_{A,FS3} - V_{R1} r_{1,R1} = 0 \quad (6)$$

$$\dot{n}_{B,FS1} + \dot{n}_{B,FS4} - \dot{n}_{B,FS2} - \dot{n}_{B,FS3} - V_{R1} (r_{1,R1} + r_{2,R1}) = 0 \quad (7)$$

$$\dot{n}_{R,FS1} + \dot{n}_{R,FS4} - \dot{n}_{R,FS2} - \dot{n}_{R,FS3} + V_{R1}(r_{1,R1} - r_{2,R1}) = 0 \quad (8)$$

$$\dot{n}_{S,FS1} + \dot{n}_{S,FS4} - \dot{n}_{S,FS2} - \dot{n}_{S,FS3} + V_{R1}r_{1,R1} = 0 \quad (9)$$

$$\dot{n}_{Y,FS1} + \dot{n}_{Y,FS4} - \dot{n}_{Y,FS2} - \dot{n}_{Y,FS3} + V_{R1}r_{2,R1} = 0 \quad (10)$$

$$\dot{n}_{Z,FS1} + \dot{n}_{Z,FS4} - \dot{n}_{Z,FS2} - \dot{n}_{Z,FS3} + V_{R1}r_{2,R1} = 0 \quad (11)$$

The design equations for reactor R1, equations (6) through (11), cannot be solved independently because they contain the unknown molar flow rates of the six species in flow stream FS2, in flow stream FS3 and in flow stream FS4. Thus there are 6 equations and 18 unknowns. Noting that the concentration of any one of the species in stream FS2 is the same as its concentration in stream FS3 (because they are both taken from the perfectly mixed contents of reactor R1), the six molar flow rates of stream FS2 can be eliminated as shown in equation (12), resulting in equations (13) through (18). This still leaves six equations with 12 unknowns, so the design equations for reactor R1 still can't be solved independently.

$$C_{i,FS2} = C_{i,FS3} \quad \Rightarrow \quad \frac{\dot{n}_{i,FS2}}{\dot{V}_{FS2}} = \frac{\dot{n}_{i,FS3}}{\dot{V}_{FS3}} \quad \Rightarrow \quad \dot{n}_{i,FS2} = \frac{\dot{V}_{FS2}}{\dot{V}_{FS3}} \dot{n}_{i,FS3} \quad (12)$$

$$\dot{n}_{A,FS1} + \dot{n}_{A,FS4} - \dot{n}_{A,FS3} \left(1 + \frac{\dot{V}_{FS2}}{\dot{V}_{FS3}} \right) - V_{R1}r_{1,R1} = 0 \quad (13)$$

$$\dot{n}_{B,FS1} + \dot{n}_{B,FS4} - \dot{n}_{B,FS3} \left(1 + \frac{\dot{V}_{FS2}}{\dot{V}_{FS3}} \right) - V_{R1}(r_{1,R1} + r_{2,R1}) = 0 \quad (14)$$

$$\dot{n}_{R,FS1} + \dot{n}_{R,FS4} - \dot{n}_{R,FS3} \left(1 + \frac{\dot{V}_{FS2}}{\dot{V}_{FS3}} \right) + V_{R1}(r_{1,R1} - r_{2,R1}) = 0 \quad (15)$$

$$\dot{n}_{S,FS1} + \dot{n}_{S,FS4} - \dot{n}_{S,FS3} \left(1 + \frac{\dot{V}_{FS2}}{\dot{V}_{FS3}} \right) + V_{R1}r_{1,R1} = 0 \quad (16)$$

$$\dot{n}_{Y,FS1} + \dot{n}_{Y,FS4} - \dot{n}_{Y,FS3} \left(1 + \frac{\dot{V}_{FS2}}{\dot{V}_{FS3}} \right) + V_{R1}r_{2,R1} = 0 \quad (17)$$

$$\dot{n}_{Z,FS1} + \dot{n}_{Z,FS4} - \dot{n}_{Z,FS3} \left(1 + \frac{\dot{V}_{FS2}}{\dot{V}_{FS3}} \right) + V_{R1}r_{2,R1} = 0 \quad (18)$$

The mole balance design equations for reactor R2 are given in equations (19) through (24). Again, the design equations for R2 cannot be solved independently because they contain the unknown molar flow rates of the six species in flow streams FS3 and in flow stream FS4. However, the combined set of

12 mole balance design equations for reactors R1 and R2, equations (13) through (24), can be solved numerically for the 12 unknown molar flow rates of the species in flow streams FS3 and FS4.

$$\dot{n}_{A,FS3} - \dot{n}_{A,FS4} - V_{R2} r_{1,R2} = 0 \quad (19)$$

$$\dot{n}_{B,FS3} - \dot{n}_{B,FS4} - V_{R2} (r_{1,R2} + r_{2,R2}) = 0 \quad (20)$$

$$\dot{n}_{R,FS3} - \dot{n}_{R,FS4} + V_{R2} (r_{1,R2} - r_{2,R2}) = 0 \quad (21)$$

$$\dot{n}_{S,FS3} - \dot{n}_{S,FS4} + V_{R2} r_{1,R2} = 0 \quad (22)$$

$$\dot{n}_{Y,FS3} - \dot{n}_{Y,FS4} + V_{R2} r_{2,R2} = 0 \quad (23)$$

$$\dot{n}_{Z,FS3} - \dot{n}_{Z,FS4} + V_{R2} r_{2,R2} = 0 \quad (24)$$

The mole balance design equations in equations (13) through (24) are nonlinear algebraic equations. The number of equations is equal to the number of unknowns, and so the equations can be solved numerically. No matter what software is used, it will be necessary to provide (a) guesses for the unknowns, and (b) code that is given values for the unknowns and uses them, along with other information given in the problem statement, to evaluate the equations, (13) through (24).

Looking at those 12 equations, it can be seen that in addition to the unknowns, they contain several quantities that are not specified in the problem statement: $\dot{n}_{A,FS1}$, $\dot{n}_{B,FS1}$, $\dot{n}_{R,FS1}$, $\dot{n}_{S,FS1}$, $\dot{n}_{Y,FS1}$, $\dot{n}_{Z,FS1}$, $r_{1,R1}$, $r_{2,R1}$, $r_{1,R2}$ and $r_{2,R2}$. Clearly, the code we write will need to calculate values for these quantities in order to evaluate equations (13) through (24). The problem statement gives the concentrations of A and B in FS1, and the concentrations of R, S, Y and Z in stream FS1 are presumably equal to zero. Since the volumetric flow rate of stream FS1 is known, the molar flow rates in stream FS1 can be computed using equation (25). The rates can be calculated using the given rate expressions, equations (26) through (29), with the necessary concentrations given in equations (30) through (35). Finally, the volume of fluid in reactor R1 is found using equation (36).

$$\dot{n}_{i,FS1} = C_{i,FS1} \dot{V}_{FS1} \quad (i = A, B, R, S, Y \text{ and } Z) \quad (25)$$

$$r_{1,R1} = k_1 C_{A,R1} C_{B,R1} \quad (26)$$

$$r_{2,R1} = k_2 C_{R,R1} C_{B,R1} \quad (27)$$

$$r_{1,R2} = k_1 C_{A,R2} C_{B,R2} \quad (28)$$

$$r_{2,R2} = k_2 C_{R,R2} C_{B,R2} \quad (29)$$

$$C_{A,R1} = \frac{\dot{n}_{A,FS3}}{\dot{V}_{FS3}} \quad (30)$$

$$C_{B,R1} = \frac{\dot{n}_{B,FS3}}{\dot{V}_{FS3}} \quad (31)$$

$$C_{R,R1} = \frac{\dot{n}_{R,FS3}}{\dot{V}_{FS3}} \quad (32)$$

$$C_{A,R2} = \frac{\dot{n}_{A,FS4}}{\dot{V}_{FS4}} \quad (33)$$

$$C_{B,R2} = \frac{\dot{n}_{B,FS4}}{\dot{V}_{FS4}} \quad (34)$$

$$C_{R,R2} = \frac{\dot{n}_{R,FS4}}{\dot{V}_{FS4}} \quad (35)$$

$$V_{R1} = V_{tot} - V_{R2} \quad (36)$$

At this point, the code to evaluate equations (13) through (24) can be written, and the equations can be solved numerically. Doing so yields the molar flow rates of the species in flow streams FS3 and FS4. Then, using equation (12) the molar flow rates in stream FS2 can be computed. Finally the conversion and selectivity can be calculated using equations (37) and (38). Upon performing the calculations, one finds that 38.7% of the A is converted and the selectivity is 1.13 mol S per mol Z. In contrast, the ideal CSTR model, without any stagnant zone predicts a conversion of 40.3% and a selectivity of 1.12 mol S per mol Z. Thus, in this particular situation, the addition of a well-mixed stagnant zone causes a subtle change in the conversion without any effect upon the selectivity.

$$f_A = \frac{\dot{n}_{A,FS1} - \dot{n}_{A,FS2}}{\dot{n}_{A,FS1}} \quad (37)$$

$$S_{\%Z} = \frac{\dot{n}_{S,FS2}}{\dot{n}_{Z,FS2}} \quad (38)$$

Calculation Details Using MATLAB

The equations to be solved in this problem are non-linear algebraic equations. As such, the MATLAB template file SolvNonDif.m can be modified and used to perform the calculations. The first modifications are shown in Listing 1. A copy of the template file was saved as Example_35_2.m. In that file the initial comment was changed to indicate that the modified version is for the solution of this example. The function name was changed to match the filename without the .m extension, and the values of all the given quantities were entered in a consistent set of units (mol, L and min). Since they are

constant, the molar flow rates of each of the species in flow stream FS1 were then calculated using equation (25).

```

% Modified version of the MATLAB template file SolvNonDif.m used in the
% solution of Example 35.2 of "A First Course on Kinetics and Reaction
% Engineering."
%
function Example_35_2
    % Known quantities and constants
    k1 = 0.0017*60; % L/mol/min
    k2 = 0.021*60; % L/mol/min
    V_total = 500; % L
    VR2 = 0.15*V_total; % L
    VR1 = V_total - VR2; % L
    CAFS1 = 2.9; % mol/L
    CBFS1 = 3.2; % mol/L
    VFRFS1 = 75.; % L/min
    VFRFS3 = 1.; % L/min
    % Calculated constants
    nAFS1 = CAFS1*VFRFS1;
    nBFS1 = CBFS1*VFRFS1;
    nRFS1 = 0;
    nSFS1 = 0;
    nYFS1 = 0;
    nZFS1 = 0;

```

Listing 1. Modified initial comment and function name and entry of known constants.

The second modification was within the internal function `evalEqns`. The function is passed values for the unknowns in a vector named `z`; the unknowns were first extracted from this vector and given names corresponding to the variables used in the solution above. The concentrations of A, B and R in each of the reactors is next calculated using equations (30) through (35). After that, the rates of reactions (1) and (2) in reactors R1 and R2 are calculated as in equations (26) through (29). Finally, the mole balance design equations (13) through (24) are evaluated and stored in the vector `f`. These modifications are shown in Listing 2.

```

function f = evalEqns(z)
    nAFS3 = z(1);
    nBFS3 = z(2);
    nRFS3 = z(3);
    nSFS3 = z(4);
    nYFS3 = z(5);
    nZFS3 = z(6);
    nAFS4 = z(7);
    nBFS4 = z(8);
    nRFS4 = z(9);
    nSFS4 = z(10);
    nYFS4 = z(11);
    nZFS4 = z(12);
    CAR1 = nAFS3/VFRFS3;
    CBR1 = nBFS3/VFRFS3;
    CRR1 = nRFS3/VFRFS3;
    CAR2 = nAFS4/VFRFS3;
    CBR2 = nBFS4/VFRFS3;
    CRR2 = nRFS4/VFRFS3;
    r1R1 = k1*CAR1*CBR1;
    r2R1 = k2*CRR1*CBR1;
    r1R2 = k1*CAR2*CBR2;
    r2R2 = k2*CRR2*CBR2;
    f = [
        nAFS1 + nAFS4 - nAFS3*(1 + VFRFS1/VFRFS3) - VR1*r1R1;
        nBFS1 + nBFS4 - nBFS3*(1 + VFRFS1/VFRFS3) - VR1*(r1R1 + r2R1);
        nRFS1 + nRFS4 - nRFS3*(1 + VFRFS1/VFRFS3) + VR1*(r1R1 - r2R1);
        nSFS1 + nSFS4 - nSFS3*(1 + VFRFS1/VFRFS3) + VR1*r1R1;
        nYFS1 + nYFS4 - nYFS3*(1 + VFRFS1/VFRFS3) + VR1*r2R1;
        nZFS1 + nZFS4 - nZFS3*(1 + VFRFS1/VFRFS3) + VR1*r2R1;
        nAFS3 - nAFS4 - VR2*r1R2;
        nBFS3 - nBFS4 - VR2*(r1R2 + r2R2);
        nRFS3 - nRFS4 + VR2*(r1R2 - r2R2);
        nSFS3 - nSFS4 + VR2*r1R2;
        nYFS3 - nYFS4 + VR2*r2R2;
        nZFS3 - nZFS4 + VR2*r2R2;
    ];
end % of internal function evalEqns

```

Listing 2. Modified version of the internal function evalEqns.

The third modification involved providing guesses for the unknowns. As can be seen in Listing 3, I guessed outlet concentrations of A and B equal to one-half of their inlet flow rates to estimate the flow of A and B in flow stream FS3. I then guessed that the flow rates of the other species in flow stream FS3 were equal to the flow of B. I guessed concentrations of A and B equal to two-tenths of their inlet flow rates to estimate the flow of A and B in flow stream FS4. I then guessed that the flow rates of the other species in flow stream FS4 were equal to the flow of B. These are just guesses, and the guesses I used are arbitrary.

```

% guesses for the solution
z_guess = [
    0.5*nAFS1*VFRFS3/VFRFS1
    0.5*nBFS1*VFRFS3/VFRFS1
    0.5*nBFS1*VFRFS3/VFRFS1
    0.5*nBFS1*VFRFS3/VFRFS1
    0.5*nBFS1*VFRFS3/VFRFS1
    0.5*nBFS1*VFRFS3/VFRFS1
    0.2*nAFS1*VFRFS3/VFRFS1
    0.2*nBFS1*VFRFS3/VFRFS1
    0.2*nBFS1*VFRFS3/VFRFS1
    0.2*nBFS1*VFRFS3/VFRFS1
    0.2*nBFS1*VFRFS3/VFRFS1
    0.2*nBFS1*VFRFS3/VFRFS1
];

```

Listing 3. Specification of guesses for the unknowns.

The final modification occurs after the equations have been solved. First the flow of A in flow stream FS2 is calculated using equation (25). Then the conversion and selectivity are calculated using equations (37) and (38). These modifications are shown in Listing 4.

```

% Solve the set of algebraic equations
z = fsolve(@evalEqns, z_guess);
display('The solver found the following values for the unknowns:');
z
display('The corresponding values of the functions being solved are
as follows:');
f = evalEqns(z)

nAFS2 = VFRFS1/VFRFS3*z(1);
pct_conversion = 100*(nAFS1 - nAFS2)/nAFS1
selectivity = z(4)/z(6)

```

Listing 4. Calculation of the conversion and selectivity after the design equations have been solved.