

# A First Course on Kinetics and Reaction Engineering

## Example 26.1

### Problem Purpose

This problem will help you determine whether you have mastered the learning objectives for this unit. It illustrates the use of all of the design equations simultaneously: mole balances, energy balance and mechanical energy (momentum) balance.

### Problem Statement

The solid catalyst for irreversible reaction (1) is in the form of pellets with a sphericity of 0.55 and a corresponding diameter of 0.25 in. When packed into a tubular reactor, the catalyst has an apparent density of 32 lbm ft<sup>-3</sup> and it packs to give a bed porosity of 0.65. A tube that is 6 m long with an inside diameter of 7 cm is going to be used as a reactor for this reaction. At the reaction conditions specified here, the overall heat transfer coefficient for this tube, based upon its inside diameter is 100 BTU h<sup>-1</sup> m<sup>-2</sup> °R<sup>-1</sup>. The tube will be fed 200 ft<sup>3</sup> h<sup>-1</sup> (65 lb<sub>m</sub> h<sup>-1</sup>) of a gas containing 15% A, 15% B and 70% I (an inert gas) at a total pressure of 5 atm and a temperature of 450 °C. The temperature on the outside of the tube will be constant and also equal to 450 °C. Reaction (1) is one-half order in A and first order in B with a pre-exponential factor of 2.9 x 10<sup>8</sup> mol h<sup>-1</sup> lbm<sup>-1</sup> atm<sup>-0.5</sup> and an activation energy of 30.2 kcal mol<sup>-1</sup>. The viscosity of the gas is approximately constant and equal to 0.3 cp. The standard heats of formation at 298K are -70, 0 and -90 kcal mol<sup>-1</sup> for A, B and Z, respectively. Their (constant) heat capacities are 12.9, 6.7 and 15.7 cal mol<sup>-1</sup> K<sup>-1</sup>, respectively, and the heat capacity of I is 5.1 cal mol<sup>-1</sup> K<sup>-1</sup>. Calculate the conversion of A, the outlet temperature and the pressure drop for this reactor.



### Problem Analysis

The problem describes a packed bed plug flow reactor operating at steady state. It does not ask us to find or test a rate expression, so it is a reaction engineering problem. The answer will require writing and solving the design equations for a steady state PFR. The reactor is not necessarily isothermal, so the design equations must include an energy balance. Also, the problem asks us to calculate the pressure drop, so the momentum balance must be included in the design equations, as well.

### Problem Solution

The following quantities are given in the problem statement:  $\Phi_S = 0.55$ ,  $D_p = 0.25$  in,  $\rho_{bed} = 32$  lbm ft<sup>-3</sup>,  $\varepsilon = 0.65$ ,  $L = 6$  m,  $D = 7$  cm,  $U = 100$  BTU h<sup>-1</sup> m<sup>-2</sup> °R<sup>-1</sup>,  $\dot{V}^0 = 200$  ft<sup>3</sup> h<sup>-1</sup>,  $\dot{m}_{tot} = 65$  lb<sub>m</sub> h<sup>-1</sup>,  $y_A^0 = 0.15$ ,  $y_B^0 = 0.15$ ,  $y_I^0 = 0.7$ ,  $P^0 = 5$  atm,  $T^0 = 450$  °C,  $T_e = 450$  °C,  $k_0 = 2.9 \times 10^8$  mol h<sup>-1</sup> lbm<sup>-1</sup> atm<sup>-0.5</sup>,  $E = 30.2$  kcal mol<sup>-1</sup>,  $\mu = 0.3$  cp,  $\Delta H_{f,A}^0(298 \text{ K}) = -70$  kcal mol<sup>-1</sup>,  $\Delta H_{f,B}^0(298 \text{ K}) = 0$  kcal mol<sup>-1</sup>,  $\Delta H_{f,Z}^0(298 \text{ K}) = -90$  kcal mol<sup>-1</sup>,  $\hat{C}_{p,A} = 12.9$  cal mol<sup>-1</sup> K<sup>-1</sup>,  $\hat{C}_{p,B} = 6.7$  cal mol<sup>-1</sup> K<sup>-1</sup>,  $\hat{C}_{p,Z} = 15.7$  cal mol<sup>-1</sup> K<sup>-1</sup>, and  $\hat{C}_{p,I} = 5.1$  cal mol<sup>-1</sup> K<sup>-1</sup>.

The information given in the problem statement allows the calculation of the inlet molar flow rates by use of the ideal gas law. By definition, the inert species does not react, so its outlet molar flow rate is equal to its inlet molar flow rate. The inlet mole percentages of A, B and I add to 100%, so there is no Z in the feed to the reactor.

$$\dot{n}_{total}^0 = \frac{P^0 \dot{V}^0}{RT^0}$$

$$\dot{n}_A^0 = 0.15 \dot{n}_{total}^0$$

$$\dot{n}_B^0 = 0.15 \dot{n}_{total}^0$$

$$\dot{n}_I^0 = 0.7 \dot{n}_{total}^0 = \dot{n}_I$$

$$\dot{n}_Z^0 = 0.0$$

These constant quantities, after conversion to consistent units (mol, m, K, h, atm), can be entered in a schematic diagram for the reactor, Figure 1.

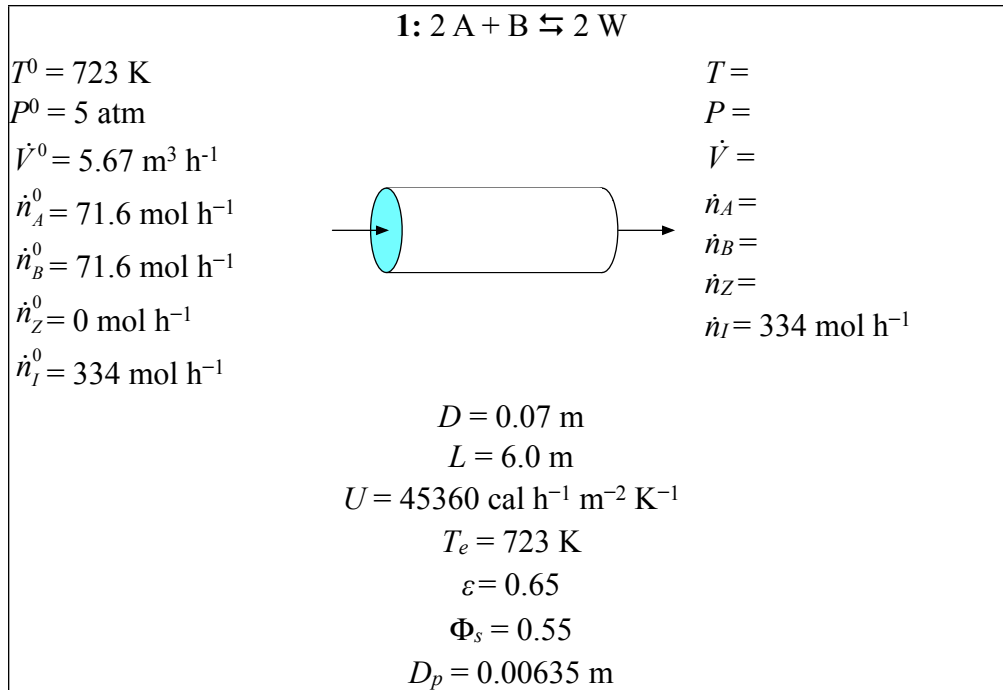


Figure 1. Schematic diagram of the packed bed PFR.

Examining the units of the pre-exponent factor show (a) that it uses partial pressures and not concentrations and (b) the rate has been normalized per unit catalyst mass. Since the design equations assume that the rate is normalized with respect to the fluid volume, the pre-exponential factor, expressed

per mass of catalyst, must be multiplied by the apparent bed density. This leads to the rate expression given in equation (2). Of course all quantities also must be converted to the same set of consistent units.

$$r_1 = \rho_{bed} k_0 \exp\left(\frac{-E}{RT}\right) P_A^{0.5} P_B \quad (2)$$

The generalized, steady state mole balance equation for species  $i$  in a PFR is given in equation (3). It can be used to generate the mole balances for each of the reactants and products as given in equations (4) through (6). In this case, there is only one reaction taking place, so the summation reduces to a single term.

$$\frac{d\dot{n}_i}{dz} = \frac{\pi D^2}{4} \left( \sum_{j=1}^{N_{rxns}} \nu_{i-j} r_j \right) \quad (3)$$

$$\frac{d\dot{n}_A}{dz} = -2 \frac{\pi D^2}{4} r_1 \quad (4)$$

$$\frac{d\dot{n}_B}{dz} = -\frac{\pi D^2}{4} r_1 \quad (5)$$

$$\frac{d\dot{n}_Z}{dz} = 2 \frac{\pi D^2}{4} r_1 \quad (6)$$

The general steady-state energy balance for a PFR is given in equation (7). Expanding the summations leads to equation (8). It is important to note that the summation in the denominator includes all species, not just the reactants and products of the reaction. The steady state mechanical energy balance for a packed bed PFR is given by equation (9).

$$\frac{dT}{dz} = \frac{\pi DU(T_e - T) - \frac{\pi D^2}{4} \left( \sum_{j=1}^{N_{reactions}} r_j \Delta H_j \right)}{\left( \sum_{i=1}^{N_{species}} \dot{n}_i \hat{C}_{p-i} \right)} \quad (7)$$

$$\frac{dT}{dz} = \frac{\pi DU(T_e - T) - \frac{\pi D^2}{4} r_1 \Delta H_1^0(T)}{\left( \dot{n}_A \hat{C}_{p,A} + \dot{n}_B \hat{C}_{p,B} + \dot{n}_W \hat{C}_{p,W} + \dot{n}_I \hat{C}_{p,I} \right)} \quad (8)$$

$$\frac{dP}{dz} = -\frac{1-\epsilon}{\epsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[ \frac{150(1-\epsilon)\mu}{\Phi_s D_p G} + 1.75 \right] \quad (9)$$

Design equations (4) through (6), (8) and (9) can be re-written in the preferred form as shown in equations (10) through (14) where each equation has a single derivative on the left of the equals sign and

a function of the independent and dependent variables on the right of the equals sign. This shows them to comprise a set of 5 ordinary differential equations (ODEs) with 5 dependent variables ( $\dot{n}_A$ ,  $\dot{n}_B$ ,  $\dot{n}_Z$ ,  $T$  and  $P$ ) and one independent variable ( $z$ ). They are initial value ODEs because the value of each of the 5 dependent variables is known at the same value ( $z_0 = 0$ ) of the independent variable. A set of  $n$  initial value ODEs containing  $n$  dependent variables and one independent variable can be solved numerically to obtain the values of all of the variables at some other point of interest. If you are not familiar with the numerical solution of initial value ODEs, Supplemental Unit S5 of “A First Course on Kinetics and Reaction Engineering” offers a brief introduction to the topic and provides MATLAB template files named SolvIVDifl.m and SolvIVDifD.m that can be used as a starting point for solving equations of this kind, if one elects to use MATLAB for that purpose.

$$\frac{d\dot{n}_A}{dz} = f_1(z, \dot{n}_A, \dot{n}_B, \dot{n}_Z, T, P) = -\frac{\pi D^2}{2} r_1; \quad \dot{n}_A(z = z_0) = \dot{n}_A^0 \quad (10)$$

$$\frac{d\dot{n}_B}{dz} = f_2(z, \dot{n}_A, \dot{n}_B, \dot{n}_Z, T, P) = -\frac{\pi D^2}{4} r_1; \quad \dot{n}_B(z = z_0) = \dot{n}_B^0 \quad (11)$$

$$\frac{d\dot{n}_Z}{dz} = f_3(z, \dot{n}_A, \dot{n}_B, \dot{n}_Z, T, P) = \frac{\pi D^2}{2} r_1; \quad \dot{n}_Z(z = z_0) = \dot{n}_Z^0 \quad (12)$$

$$\frac{dT}{dz} = f_4(z, \dot{n}_A, \dot{n}_B, \dot{n}_Z, T, P) = \frac{\pi D U (T_e - T) - \frac{\pi D^2}{4} r_1 \Delta H_1^0(T)}{(\dot{n}_A \hat{C}_{p,A} + \dot{n}_B \hat{C}_{p,B} + \dot{n}_Z \hat{C}_{p,Z} + \dot{n}_I \hat{C}_{p,I})}; \quad (13)$$

$$T(z = z_0) = T^0$$

$$\frac{dP}{dz} = f_5(z, \dot{n}_A, \dot{n}_B, \dot{n}_Z, T, P) = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[ \frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75 \right] \quad (14)$$

$$P(z = z_0) = P^0$$

Generally, no matter what software package is used, the numerical solution of these equations will require you to provide (a) the initial values ( $z_0$ ,  $\dot{n}_A^0$ ,  $\dot{n}_B^0$ ,  $\dot{n}_Z^0$ ,  $T^0$  and  $P^0$ ), (b) the final value of either the independent variable or one of the dependent variables at the point of interest and (c) code that, given values for the independent and dependent variables, evaluates the functions  $f_1$  through  $f_5$  in equations (10) through (14).

The initial values (at  $z = z_0 = 0$ ) needed to solve the design equations ( $\dot{n}_A^0$ ,  $\dot{n}_B^0$ ,  $\dot{n}_Z^0$ ,  $T^0$  and  $P^0$ ) are given in Figure 1. The known final value is the length of the reactor ( $z = z_f = L = 6$  m). Looking at the functions  $f_1$  through  $f_5$ , it can be seen that the following quantities are either universal constants or constants whose values have already been listed:  $\pi$ ,  $D$ ,  $U$ ,  $T_e$ ,  $\hat{C}_{p,A}$ ,  $\hat{C}_{p,B}$ ,  $\hat{C}_{p,Z}$ ,  $\hat{C}_{p,I}$ ,  $\dot{n}_I$ ,  $\varepsilon$ ,  $\Phi_s$ ,  $D_p$ ,  $g_c$  and  $\mu$ .

Only  $r_1$ ,  $\Delta H_1^0(T)$ ,  $G$  and  $\rho$  have not yet been specified, so the code to evaluate the functions  $f_1$  through  $f_5$  will need to calculate these quantities before it can evaluate the functions. The rate,  $r_1$ , is calculated using equation (2) where  $k_0$ ,  $E$ ,  $\rho_{bed}$  and  $R$  are known or given constants and where the partial pressures are calculated using equations (15) and (16). In equations (15) and (16),  $\dot{n}_I$  is a known constant while  $\dot{n}_A$ ,  $\dot{n}_B$ ,  $\dot{n}_Z$  and  $P$  are dependent variables and therefore will be given as input to the code.

$$P_A = \frac{\dot{n}_A}{\dot{n}_A + \dot{n}_B + \dot{n}_Z + \dot{n}_I} P \quad (15)$$

$$P_B = \frac{\dot{n}_B}{\dot{n}_A + \dot{n}_B + \dot{n}_Z + \dot{n}_I} P \quad (16)$$

To calculate  $\Delta H_1^0(T)$ , the standard heat of reaction at 298 K must first be calculated using equation (17). The standard heats of formation at 298 K seen in equation (17) are given in the problem statement and the stoichiometric coefficients can be determined from the balanced reaction, equation (1). The standard heat of reaction at any temperature,  $T$ , is then calculated using that result and equation (18), where the heat capacities are taken to be constant with values given in the problem statement. The temperature is a dependent variable and therefore will be given as input to the code.

$$\begin{aligned} \Delta H_1^0(298 \text{ K}) &= \sum_{i=1}^{N_{\text{species}}} (v_{i,1} \Delta H_{f,i}^0(298 \text{ K})) \\ &= v_{A,1} \Delta H_{f,A}^0(298 \text{ K}) + v_{B,1} \Delta H_{f,B}^0(298 \text{ K}) + v_{Z,1} \Delta H_{f,Z}^0(298 \text{ K}) \\ &= 2\Delta H_{f,Z}^0(298 \text{ K}) - 2\Delta H_{f,A}^0(298 \text{ K}) - \Delta H_{f,B}^0(298 \text{ K}) \end{aligned} \quad (17)$$

$$\begin{aligned} \Delta H_1^0(T) &= \Delta H_1^0(298 \text{ K}) + \sum_{i=1}^{N_{\text{species}}} \left( v_{i,1} \int_{298 \text{ K}}^T \hat{C}_{p,i} dT \right) \\ &= \Delta H_1^0(298 \text{ K}) + 2 \int_{298 \text{ K}}^T \hat{C}_{p,Z} dT - 2 \int_{298 \text{ K}}^T \hat{C}_{p,A} dT - \int_{298 \text{ K}}^T \hat{C}_{p,B} dT \\ &= \Delta H_1^0(298 \text{ K}) + (2\hat{C}_{p,Z} - 2\hat{C}_{p,A} - \hat{C}_{p,B})(T - 298 \text{ K}) \end{aligned} \quad (18)$$

The mass velocity can be calculated using equation (19) where the (constant) mass flow rate and tube diameter are known constants. Noting that the mass flow rate will not change as reaction occurs, the fluid density,  $\rho$ , can be calculated using equation (20) where the gas constant, the mass flow rate and molar flow rate of I are known constants and the other quantities ( $\dot{n}_A$ ,  $\dot{n}_B$ ,  $\dot{n}_Z$ ,  $T$  and  $P$ ) are dependent variables that will be given as input to the code.

$$G = \frac{4\dot{m}_{tot}}{\pi D^2} \quad (19)$$

$$\rho = \frac{\dot{m}_{tot}}{\dot{V}} = \frac{\dot{m}_{tot} P}{RT(\dot{n}_A + \dot{n}_B + \dot{n}_Z + \dot{n}_I)} \quad (20)$$

Thus the input and code necessary for numerical solution of the design equations are available and equations (10) through (14) can be solved numerically to find the values of  $\dot{n}_A$ ,  $\dot{n}_B$ ,  $\dot{n}_Z$ ,  $T$  and  $P$  at the reactor outlet ( $z = L = 6$  m). The conversion of A can then be computed using equation (21). Similarly, the pressure drop can be calculated using equation (22). Upon doing so, one finds that the outlet temperature is 725 K, the fractional conversion of A is 0.103 and the pressure drop is 0.073 atm.

$$f_A = \frac{\dot{n}_A^0 - \dot{n}_A}{\dot{n}_A^0} \quad (21)$$

$$-\Delta P = P^0 - P \quad (22)$$

### Calculation Details Using MATLAB

If you elect to use MATLAB to solve the design equations, Supplemental Unit S5 provides template files that can be used. In this problem, the equations are initial value ODEs and the final value of the independent variable is provided, so the appropriate template file is SolvIVDifl.m. Before that file can be used, you must make four required modifications. Here I will also describe a few non-required modifications that you might want to consider when solving problems of this type.

To begin, I made a copy of the template file and saved it as Example\_26\_1.m; a copy of that file accompanies this solution. Since the function name must match the filename, I changed the name of the function to Example\_26\_1. At the same time, knowing that I won't need to use the results from these calculations in subsequent calculations, I changed the function so that it does not return any values, but instead prints them out. The template file begins with a long set of comments describing what it does and how to use it; I replaced these comments with a brief comment stating the purpose of the modified version. None of these modifications were required. The first required modification involves entering all the known quantities from the problem statement along with universal constants that will be needed (from handbooks or other reference sources). As these were entered, they were converted to a consistent set of units. The result of making all these modifications is shown in Listing 1.

```

% Modified version of the MATLAB template file SolvIVDifI.m used in the
% solution of Example 26.1 of "A First Course on Kinetics and Reaction
% Engineering."
%
function Example_26_1
    % Known quantities and constants
    sp = 0.55;
    Dp = 0.25 * 0.0254; % m
    rho = 32 / 0.02832; % lbm/m^3
    eps = 0.65;
    L = 6; % m
    D = 7 / 100; % m
    U = 100 * 251.996/1.8; % cal/(h m^2 K)
    VFR0 = 200 * 0.02832; % m^3/h
    m0 = 65; % lbm/h
    yA0 = 0.15;
    yB0 = 0.15;
    yI0 = 0.7;
    P0 = 5; % atm
    T0 = 450 + 273.15; % K
    Te = 450 + 273.15; % K
    k0 = 2.9E8; % mol/(h lbm atm^0.5)
    E = 30200; % cal/mol
    mu = 0.3 * 2.41909 / 0.3048; % lbm/(m h)
    dHfA = -70000; % cal/mol
    dHfB = 0; % cal/mol
    dHfZ = -90000; % cal/mol
    CpA = 12.9; % cal/(mol K)
    CpB = 6.7; % cal/(mol K)
    CpZ = 15.7; % cal/(mol K)
    CpI = 5.1; % cal/(mol K)
    % Universal Constants
    Re = 1.987; % cal/(mol K)
    Rpv = 0.08206E-3; % m3 atm/(mol K)
    gc = 32.174*2116.2*60^2*60^2/.3048; % lbm/(m h^2 atm)
    % Additional Calculated Constants
    ntot0 = P0*VFR0/Rpv/T0; % mol/h, ideal gas law
    nA0 = yA0*ntot0; % mol/h
    nB0 = yB0*ntot0; % mol/h
    nI0 = yI0*ntot0; % mol/h
    nI = nI0; % mol/h
    nZ0 = 0; % mol/h
    dH298 = 2*dHfZ - 2*dHfA - dHfB; % cal/mol, equation (17)
    G = 4*m0/pi()/D^2; % lbm/(m^2 h), equation (19)

```

Listing 1. Initial comment, function declaration and known constants after modification of SolvIVDifI.m

The second required modification involves entering code that, given values for the independent and dependent variables, evaluates the functions  $f_1$  through  $f_5$  in equations (10) through (14). Notice that the equations are provided as a vector quantity. Thus, it is necessary to map the dependent variables used in the problem statement ( $\dot{n}_A$ ,  $\dot{n}_B$ ,  $\dot{n}_Z$ ,  $T$  and  $P$ ) to a vector  $z$ , and the corresponding derivatives are mapped

to a vector  $dzdt$ . (Don't be confused: **in the template file  $z$  represents the vector of dependent variables and  $t$  represents the independent variable whereas in our problem,  $z$  is the variable used for the independent variable**. In other words, the independent variable,  $z$ , used in the problem statement maps to the variable  $t$  in the MATLAB code.) I find it useful at the start of the internal function that will evaluate the derivatives (odeqns), to define local variables with the names used in the problem statement. This modification is not required, but in my opinion, it makes the code more readable and easier to debug. In addition, the resulting list of variables serves as a reminder of the mapping of the problem statement variables to the vector  $z$ . The required code first calculates the two reactant partial pressures according to equations (15) and (16). Following that, the rate is calculated using equation (2), the heat of reaction is calculated using equation (18) and the fluid density is calculated using equation (20). Finally, the functions  $f_1$  through  $f_5$  are evaluated using equations (10) through (14), saving the results in the vector  $dzdt$  using the same mapping that was used to map the dependent variables to the vector  $z$ . The resulting code is shown in Listing 2.

```

% Function that evaluates the ODEs
function dzdt = odeqns(t,z)
    nA = z(1);
    nB = z(2);
    nZ = z(3);
    T = z(4);
    P = z(5);
    PA = nA*P/(nA + nB + nZ + nI); % equation (15)
    PB = nB*P/(nA + nB + nZ + nI); % equation (16)
    r1 = rho*k0*exp(-E/Re/T)*PA^0.5*PB; % equation (2)
    dH = dH298 + (2*CpZ - 2*CpA - CpB)*(T - 298); % equation (18)
    rho = m0*P/Rpv/T/(nA + nB + nZ + nI); % lbm/m^3, equation (20)
    dzdt = [
        -pi()*D^2/2*r1;
        -pi()*D^2/4*r1;
        pi()*D^2/2*r1;
        (pi()*D*U*(Te-T) - pi()*D^2/4*r1*dH)/(nA*CpA + nB*CpB + nZ*CpZ +
nI*CpI);
        -(1-eps)/eps^3*G^2/rho/sp/Dp/gc*(150*(1-eps)*mu/sp/Dp/G + 1.75);
    ];
end % of internal function odeqns

```

Listing 2. Results of the second required modification.

The third required modification involves providing the initial values of the independent and dependent variables and the final value of the independent variable. Recall that the independent variable,  $z$ , from the problem statement maps to the variable  $t$  in the code. Thus  $t_0$  in the code is set equal to the initial value of the axial position, which is denoted as  $z_0 = 0$  in the problem statement. The initial values of



the dependent variables are entered as a vector named  $z_0$ , and they must use the same mapping of the problem variables ( $\dot{n}_A^0, \dot{n}_B^0, \dot{n}_Z^0, T^0$  and  $P^0$ ) to the vector  $z_0$  as was used previously to map ( $\dot{n}_A, \dot{n}_B, \dot{n}_Z, T$  and  $P$ ) to  $z$ . As with the initial value, the final value,  $z_f$  in the problem statement, maps to  $t_f$  in the code. The results of performing this modification are shown in Listing 3.

```
% Initial and final values
t0 = 0;
z0 = [
    nA0
    nB0
    nZ0
    T0
    P0
];
tf = L;
```

*Listing 3. Results of the third required modification.*

The fourth and final required modification is to use the results from solving the ODEs to calculate whatever the problem requested. After solution, the vector  $z$  contains the final values of the dependent variables, using the same mapping as in Listing 2. Thus, the outlet temperature is equal to  $z(4)$ , but the problem also asked for the outlet conversion and the pressure drop. Code was added therefore to calculate the percent conversion and the pressure drop using equations (21) and (22), as shown in Listing 4.

```
% Calculate and display the requested results
T_outlet_Kelvin = z(4)
pct_conv = 100*(nA0-z(1))/nA0
P_drop_atm = P0 - z(5)
```

*Listing 4. Results of the fourth required modification.*

Once the file containing all the modifications had been saved, it was executed by typing Example\_26\_1 at the MATLAB command prompt. Doing so generated the output shown in Listing 5.

```
>> Example_26_1

T_outlet_Kelvin =
    723.2290

pct_conv =
    0.1022

P_drop_atm =
    0.0733
```

*Listing 5. Output produced upon execution of the modified file.*