March 31, 2017

1. A second order liquid phase reaction occurs in an adiabatic PFR. The reaction and rate expressions are:

$$A + B \rightarrow C + D \qquad (-r_A) = k C_A C_B \quad \frac{mol}{m^3 s} \qquad k = 1.0 \times 10^{-5} \exp\left(\frac{-1000}{T}\right)$$

where the temperature, T, is in Kelvin. The total feed to the reactor is 100 mol/s and is composed of 50% A and 50% B. The concentrations of A and B in the feed are 1000 mol/m^3. The feed temperature is 300 K. The enthalpy of reaction at 300 K is $(-\Delta H_{R,300}) = 50,000 \frac{J}{mol}$ (exothermic reaction). The heat capacities for the four species are:

$$C_{P,A} = 75 \frac{J}{mol \cdot K}, \quad C_{P,B} = 70 \frac{J}{mol \cdot K}, \quad C_{P,C} = 80 \frac{J}{mol \cdot K}, \quad C_{P,D} = 75 \frac{J}{mol \cdot K},$$

(a) Calculate the temperature of the stream in the reactor when the fractional conversion is 0.50.
(b) Calculate the reactor volume required to reach 50 % conversion.

2. A tubular flow reactor is to be designed to produce butadiene from butene by dehydrogenation (gas phase reaction). The first order reaction rate expression is written in terms of the partial pressure of butene as:

$$C_4H_8 \rightarrow C_4H_6 + H_2 \qquad (-r_{C_4H_8}) = k P_{C_4H_8} \quad \frac{mol}{L \cdot h}$$
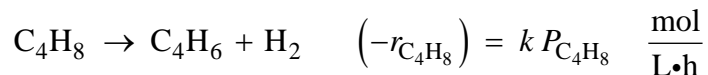
The constant k has units of $mol \cdot (h \cdot L \cdot atm)^{-1}$. Note the units on the rate constant, because the rate is given interms of partial pressure of butane. The reaction is endothermic, the reactor is often operated adiabatically, therefore steam is often added to the feed to provide thermal energy for the reaction. For this reactor, the feed is a mixture of 10 mol of steam for each mol of butene. The reactor pressure is 2 atm and the feed temperature is 650°C. Values of the rate constant at different temperatures are given in the table following.

T, K	922	900	877	855	832
k	11.0	4.90	2.04	0.85	0.32

Assume that the heat of reaction is a constant 1.1 x 10^5 J/mol butene. The heat capacity of the feed stream may be considered constant at 2.1 kJ/kg·K.

a) Calculate the reactor volume for a 20% conversion of butene if the reactor is operated isothermally at 650°C with a total inlet molar flow rate of 11,000 mol/h.
b) Determine the reactor volume for 20% conversion of butene for a total inlet molar feed rate of 11,000 mol/h in an adiabatic reactor.

Solution to problem 1

The reaction occurs in an adiabatic reactor. We want to know the temperature when the conversion is 0.50, therefore we must develop a relationship between temperature and conversion. The general formula for the adiabatic reaction line is:

$$\sum_{i=1}^{n} F_i C_{Pi} \frac{dT}{dV} = (-\Delta H_R) F_{A0} \frac{dX_A}{dV}$$

Or, by eliminating the volume differential:

$$\sum_{i=1}^{n} F_i C_{Pi} \, dT = (-\Delta H_R) F_{A0} \, dX_A$$

We can analyze each piece of the equation:

$$\sum_{i=1}^{n} F_i C_{Pi} = F_{A0}(1-X_A)C_{P,A} + F_{B0}(1-X_A)C_{P,B} + F_{A0}X_A C_{P,C} + F_{A0}X_A C_{P,D}$$

Substitute the numbers:

$$\sum_{i=1}^{n} F_i C_{Pi} = (50)(75)(1-X_A) + (50)(70)(1-X_A) + (50)(80)X_A + (50)(75)X_A$$

$$\sum_{i=1}^{n} F_i C_{Pi} = 7250 + 500X_A$$

The enthalpy of reaction depends on the temperature, according to:

$$\frac{\partial(\Delta H_R)}{\partial T} = \Delta C_P = (C_P)_{\text{products}} - (C_P)_{\text{reactants}} = (75+80) - (75+70) = 10$$

Therefore:

$$\Delta H_R = \Delta H_{R,300} + \int_{300}^{T} 10 \, dT = (-50,000) + (10T - 3000) = -53000 + 10T$$

Substitute into the adiabatic reaction line:

$$(7250 + 500X_A) dT = (53000 - 10T) 50 \, dX_A$$

Rearrange:

$$\frac{dT}{(5300 - T)} = \frac{dX_A}{(14.5 + X_A)}$$

Integrate:

$$-\ln\left(5300 - T\right)\big|_{300}^{T} = \ln\left(14.5 + X_A\right)\big|_{0}^{0.5}$$

Substitute the limits:

$$\left(\frac{5000}{5300 - T}\right) = \left(\frac{14.5 + 0.5}{14.5}\right)$$

Solve for $T = 466.67$ K.

To find the elapsed time, we must solve the mole balance equation. The first step is to express the energy balance in the general form:

$$-\ln\left(5300 - T\right)\big|_{300}^{T} = \ln\left(14.5 + X_A\right)\big|_{0}^{X_A}$$

$$\left(\frac{5000}{5300 - T}\right) = \left(\frac{14.5 + X_A}{14.5}\right)$$

Simplify:

$$\left(\frac{5300 - T}{5000}\right) = \left(\frac{14.5}{14.5 + X_A}\right)$$

$$5300 - \left(\frac{72\,500}{14.5 + X_A}\right) = T$$

The mole balance i is:

$$F_{A0}\frac{d\,X_A}{d\,V} = \left(-r_A\right) = 1.0\times10^{-5}\exp\left(\frac{-1000}{T}\right)C_{A0}^2\left(1 - X_A\right)^2$$

Substitute for T and the other values:

$$\frac{d\,X_A}{d\,V} = 0.2\exp\left(\frac{-1000}{5300 - \left(\dfrac{72\,500}{14.5 + X_A}\right)}\right)\left(1 - X_A\right)^2$$

Integrate numerically, from zero conversion to 50 %. The final volume is sought so a trial and error solution is required. The answer is 65.4 m^3.

Solution to problem 2

The rate constant as a function of temperature may be calculated from the data provided to give:

$$k = 1.666 \times 10^{15} \exp\left(\frac{-30109}{T}\right) \frac{mol}{h \cdot L \cdot atm}$$

The rate is first order in butene partial pressure:

$$(-r_A) = k P_A$$

The reactor is a constant pressure plug flow reactor. The change in moles on reaction must be considered. The partial pressure of A (butene) is given by

$$P_A = Y_A P_t$$

where P_t is the reactor pressure and y_A is the mole fraction. Build the stoichiometric table

Compound	Moles Initial	Moles Final
C_4H_8	F_{A0}	$F_{A0}(1 - X_A)$
H_2O	$10 F_{A0}$	$10 F_{A0}$
H_2	0	$F_{A0}X_A$
C_4H_6	0	$F_{A0}X_A$
Total	$11 F_{A0}$	$(11 + X_A) F_{A0}$

The partial pressure of A is therefore:

$$P_A = Y_A P_t = \frac{(1 - X_A)}{11 + X_A} P_t$$

For isothermal operation at 650°C, the rate constant is calculated to be $k = 11.4 \frac{mol}{h \cdot L \cdot atm}$. The mole balance equation is:

$$\frac{V}{F_{A0}} = \int_0^X \frac{d X_A}{(-r_A)}$$

The total molar feedrate is $11,000 \frac{mol}{h}$. Therefore, the molar flow rate of A is $F_{A0} = 1000 \frac{mol}{h}$. The reactor pressure is 2 atm, so substitution gives:

$$V = 1000 \frac{\text{mol}}{\text{h}} \int_0^{0.2} \frac{d X_A}{11.4 \frac{\text{mol}}{\text{h} \cdot \text{L} \cdot \text{atm}} \left(\frac{1 - X_A}{11 + X_A} \right) 2 \, \text{atm}} = 43.86 \int_0^{0.2} \left(\frac{11 + X_A}{1 - X_A} \right) d X_A$$

Integrating analytically gives:

$$V = 43.86 \left[-11 \left(\ln (1 - X_A) \right) + 1 - X_A - \ln (1 - X_A) \right]_0^{0.2}$$

Solving gives $V = 108.7 \, \text{L}$. For adiabatic operation, the energy balance must be solved. The equation is:

$$\dot{m} C_P (T - T_0) = \Delta H_{R,A} (F_A - F_{A0}) = \left(-\Delta H_{R,A} \right) F_{A0} X_A$$

Rearrange explicitly in T.

$$T = \frac{F_{A0}}{\dot{m} C_P} (-\Delta H_R) X + T_0$$

The data are: $\Delta H_R = 1.1 \times 10^5 \, \dfrac{\text{J}}{\text{mol}}$ and $C_P = 2100 \, \dfrac{\text{J}}{\text{kg} \cdot \text{K}}$

The mass flow rate of the feed can be computed:

$$\dot{m} = F_{C_4 H_8} \times M_{C_4 H_8} + F_{H_2 O} \times M_{H_2 O}$$

$$\dot{m} = 1000 \frac{\text{mol}}{\text{h}} \times 56 \frac{\text{g}}{\text{mol}} \times 10^{-3} \frac{\text{kg}}{\text{g}} + 10{,}000 \times 18 \frac{\text{g}}{\text{mol}} \times 10^{-3} \frac{\text{kg}}{\text{g}}$$

$$\dot{m} = 236 \frac{\text{kg}}{\text{h}}$$

Substitute into the heat balance:

$$T = 923 - 222 X_A$$

Substitution of the energy balance into the mole balance gives:

$$V = 1000 \frac{\text{mol}}{\text{h}} \int_0^{0.2} \frac{(11 + X_A)}{1.666 \times 10^{15} \frac{\text{mol}}{\text{h} \cdot \text{L} \cdot \text{atm}} 2 \, \text{atm} \exp \left(\frac{-30109}{923 - 222 X} \right) (1 - X_A)} d X_A$$

$$V = 3 \times 10^{-13} \int_0^{0.2} \frac{(11 + X_A)}{(1 - X) \exp \left(\dfrac{-30109}{923 - 222 X_A} \right)} d X_A$$

The integral is solved numerically to give $V = 283.4 \, \text{L}$