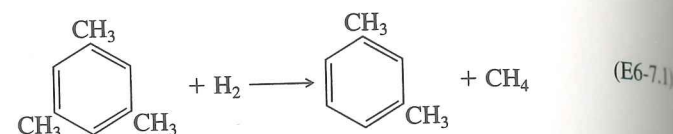
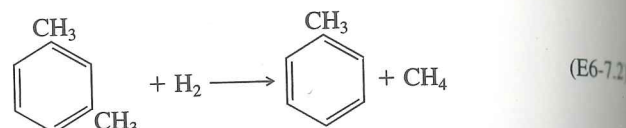


Example 6-7 Hydrodealkylation of Mesitylene in a PFR

The production of *m*-xylene by the hydrodealkylation of mesitylene over a Houdry Detrol catalyst⁵ involves the following reactions:



m-Xylene can also undergo hydrodealkylation to form toluene:



A significant economic incentive

The second reaction is undesirable, because *m*-xylene sells for a higher price than toluene (\$1.32/lb_m vs. \$0.30/lb_m).⁶ Thus we see that there is a significant incentive to maximize the production of *m*-xylene.

The hydrodealkylation of mesitylene is to be carried out isothermally at 1500°R and 35 atm in a packed-bed reactor in which the feed is 66.7 mol% hydrogen and 33.3 mol% mesitylene. The volumetric feed rate is 476 ft³/h and the reactor volume (i.e., $V = W/\rho_b$) is 238 ft³.

The rate laws for reactions 1 and 2 are, respectively,

$$-r_{1M} = k_1 C_M C_H^{0.5} \quad (\text{E6-7.3})$$

$$r_{2T} = k_2 C_X C_H^{0.5} \quad (\text{E6-7.4})$$

where the subscripts are: M = mesitylene, X = *m*-xylene, T = toluene, Me = methane, and H = hydrogen (H₂).

At 1500°R, the specific reaction rates are

$$\text{Reaction 1: } k_1 = 55.20 \text{ (ft}^3/\text{lb mol)}^{0.5}/\text{h}$$

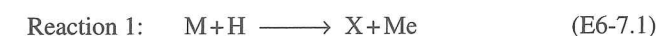
$$\text{Reaction 2: } k_2 = 30.20 \text{ (ft}^3/\text{lb mol)}^{0.5}/\text{h}$$

The bulk density of the catalyst has been included in the specific reaction rate (i.e., $k_1 = k'_1 \rho_b$).

Plot the concentrations of hydrogen, mesitylene, and xylene as a function of space time. Calculate the space time where the production of xylene is a maximum (i.e., τ_{opt}).

⁵ Ind. Eng. Chem. Process Des. Dev., 4, 92 (1965); 5, 146 (1966).

⁶ November 2004 prices, from Chemical Market Reporter (Schnell Publishing Co.) 265, 23 (May 17, 2004). Also see www.chemweek.com/ and www.icislor.com

Solution**1. Mole balances:**

$$\text{Hydrogen: } \frac{dF_H}{dV} = r_H \quad (\text{E6-7.5})$$

$$\text{Mesitylene: } \frac{dF_M}{dV} = r_M \quad (\text{E6-7.6})$$

$$\text{Xylene: } \frac{dF_X}{dV} = r_X \quad (\text{E6-7.7})$$

$$\text{Toluene: } \frac{dF_T}{dV} = r_T \quad (\text{E6-7.8})$$

$$\text{Methane: } \frac{dF_{\text{Me}}}{dV} = r_{\text{Me}} \quad (\text{E6-7.9})$$

2. Rate laws and net rates: Given

$$\text{Reaction 1: } -r_{1M} = k_1 C_H^{1/2} C_M \quad (\text{E6-7.3})$$

$$\text{Reaction 2: } r_{2T} = k_2 C_H^{1/2} C_X \quad (\text{E6-7.4})$$

Relative rates:

$$(1) \quad -r_{1H} = -r_{1M} = r_{1\text{Me}} = r_{1X} \quad (\text{E6-7.10})$$

$$(2) \quad r_{2T} = r_{2\text{Me}} = -r_{2H} = -r_{2X} \quad (\text{E6-7.11})$$

Net rates:

$$r_M = r_{1M} = -k_1 C_H^{1/2} C_M \quad (\text{E6-7.12})$$

$$r_H = r_{1H} + r_{2H} = r_{1H} - r_{2T} = -k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X \quad (\text{E6-7.13})$$

$$r_X = r_{1X} + r_{2X} = -r_{1H} - r_{2T} = k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X \quad (\text{E6-7.14})$$

$$r_{\text{Me}} = r_{1\text{Me}} + r_{2\text{Me}} = -r_{1H} + r_{2T} = k_1 C_H^{1/2} C_M + k_2 C_H^{1/2} C_X \quad (\text{E6-7.15})$$

$$r_T = r_{2T} = k_2 C_H^{1/2} C_X \quad (\text{E6-7.16})$$

3. Stoichiometry

The volumetric flow rate is

$$v = v_0 \frac{F_T P_0 T}{F_{T0} P T_0}$$

Mole balance on each and every species

Because there is no pressure drop $P = P_0$ (i.e., $y = 1$), the reaction is carried out isothermally, $T = T_0$, and there is no change in the total number of moles; consequently,

$$v = v_0$$

Flow rates:

$$F_H = v_0 C_H \quad (\text{E6-7.17})$$

$$F_M = v_0 C_M \quad (\text{E6-7.18})$$

$$F_X = v_0 C_X \quad (\text{E6-7.19})$$

$$F_{Me} = v_0 C_{Me} = F_{H0} - F_H = v_0 (C_{H0} - C_H) \quad (\text{E6-7.20})$$

$$F_T = F_{M0} - F_M - F_X = v_0 (C_{M0} - C_M - C_X) \quad (\text{E6-7.21})$$

4. **Combining** and substituting in terms of the space-time yields

$$\tau = \frac{V}{v_0}$$

If we know C_M , C_H , and C_X , then C_{Me} and C_T can be calculated from the reaction stoichiometry. Consequently, we need only to solve the following three equations:

$$\frac{dC_H}{d\tau} = -k_1 C_H^{1/2} C_M - k_2 C_X C_H^{1/2} \quad (\text{E6-7.22})$$

$$\frac{dC_M}{d\tau} = -k_1 C_M C_H^{1/2} \quad (\text{E6-7.23})$$

$$\frac{dC_X}{d\tau} = k_1 C_M C_H^{1/2} - k_2 C_X C_H^{1/2} \quad (\text{E6-7.24})$$

5. Parameter evaluation:

At $T_0 = 1,500^\circ \text{R}$ and $P_0 = 35 \text{ atm}$, the total concentration is

$$C_{T0} = \frac{P_0}{RT_0} = \frac{35 \text{ atm}}{\left(0.73 \frac{\text{atm ft}^3}{\text{lb mol} \cdot ^\circ \text{R}}\right)(1,500^\circ \text{R})} = 0.032 \text{ lb mol/ft}^3$$

$$C_{H0} = y_{H0} C_{T0} = (0.667)(0.032 \text{ lb mol/ft}^3) = 0.021 \text{ lb mol/ft}^3$$

$$C_{M0} = \frac{1}{2} C_{H0} = 0.0105 \text{ lb mol/ft}^3$$

$$C_{X0} = 0$$

$$\tau = \frac{V}{v_0} = \frac{238 \text{ ft}^3}{476 \text{ ft}^3/\text{h}} = 0.5 \text{ h}$$

The emergence of user-friendly *ODE solvers* favors this approach over fractional conversion.

$$F_{T0} = C_{T0} v_0 = \left(0.032 \frac{\text{lb mol}}{\text{ft}^3}\right) \left(476 \frac{\text{ft}^3}{\text{h}}\right)$$

$$F_{T0} = 15.23 \text{ mol/h}$$

We now solve these three equations, (E6-7.22) to (E6-7.24), simultaneously using Polymath. The program and output in graphical form are shown in Table E6-7.1 and Figure E6-7.1, respectively. However, I hasten to point out that these equations can be solved analytically and the solution was given in the first edition of this text.

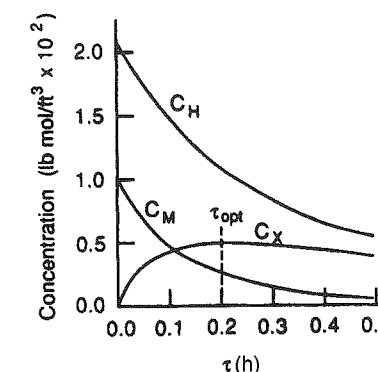


Figure E6-7.1 Concentration profiles in a PFR.

TABLE E6-7.1 POLYMATH PROGRAM

ODE Report (RKF45)

Differential equations as entered by the user

- [1] $d(C_H)/d(\tau) = r1h + r2h$
- [2] $d(C_M)/d(\tau) = r1m$
- [3] $d(C_X)/d(\tau) = r1x + r2x$

Explicit equations as entered by the user

- [1] $k1 = 55.2$
- [2] $k2 = 30.2$
- [3] $r1m = -k1 * C_m * (C_h^{.5})$
- [4] $r2t = k2 * C_x * (C_h^{.5})$
- [5] $r1h = r1m$
- [6] $r2m = -r2t$
- [7] $r1x = -r1m$
- [8] $r2x = -r2t$
- [9] $r2h = -r2t$



Example Problem

6.6 Multiple Reactions in a CSTR

For a CSTR, a coupled set of algebraic equations analogous to PFR differential equations must be solved.

$$V = \frac{F_{j0} - F_j}{-r_j} \quad (6-28)$$

Example 6-10 Calculating Concentrations as Functions of Position for NH_3 Oxidation in a PFR

The following gas-phase reactions take place simultaneously on a metal oxide-supported catalyst:

1. $4\text{NH}_3 + 5\text{O}_2 \longrightarrow 4\text{NO} + 6\text{H}_2\text{O}$
2. $2\text{NH}_3 + 1.5\text{O}_2 \longrightarrow \text{N}_2 + 3\text{H}_2\text{O}$
3. $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$
4. $4\text{NH}_3 + 6\text{NO} \longrightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$

Writing these equations in terms of symbols yields



with⁸

$$k_{1A} = 5.0 \text{ (m}^3/\text{kmol)}^2/\text{min} \quad k_{2A} = 2.0 \text{ m}^3/\text{kmol} \cdot \text{min}$$

$$k_{3B} = 10.0 \text{ (m}^3/\text{kmol)}^2/\text{min} \quad k_{4C} = 5.0 \text{ (m}^3/\text{kmol)}^{2/3}/\text{min}$$

Note: We have converted the specific reaction rates to a per unit volume basis by multiplying the k' on a per mass of catalyst basis by the bulk density of the packed bed (i.e., $k = k' \rho_B$).

Determine the concentrations as a function of position (i.e., volume) in a PFR.

Additional information: Feed rate = 10 dm³/min; volume of reactor = 10 dm³; and

$$C_{A0} = C_{B0} = 1.0 \text{ mol/dm}^3, \quad C_{T0} = 2.0 \text{ mol/dm}^3$$

Solution

Mole balances:

$$\text{Species A: } \frac{dF_A}{dV} = r_A \quad (\text{E6-10.5})$$

$$\text{Species B: } \frac{dF_B}{dV} = r_B \quad (\text{E6-10.6})$$

$$\text{Species C: } \frac{dF_C}{dV} = r_C \quad (\text{E6-10.7})$$

⁸ Reaction orders and rate constants were estimated from periscosity measurements at a bulk catalyst density of 1.2 kg/dm³.

Solutions to these equations are most easily obtained with an ODE solver

$$\text{Species D: } \frac{dF_D}{dV} = r_D \quad (\text{E6-10.8})$$

$$\text{Species E: } \frac{dF_E}{dV} = r_E \quad (\text{E6-10.9})$$

$$\text{Species F: } \frac{dF_F}{dV} = r_F \quad (\text{E6-10.10})$$

$$\text{Total: } F_T = F_A + F_B + F_C + F_D + F_E + F_F \quad (\text{E6-10.11})$$

Rate laws: See above for r_{1A} , r_{2A} , r_{3B} , and r_{4C} .

Stoichiometry:

A. *Relative rates*

$$\text{Reaction 1: } \frac{r_{1A}}{-4} = \frac{r_{1B}}{-5} = \frac{r_{1C}}{4} = \frac{r_{1D}}{6} \quad (\text{E6-10.12})$$

$$\text{Reaction 2: } \frac{r_{2A}}{-2} = \frac{r_{2B}}{-1.5} = \frac{r_{2E}}{1} = \frac{r_{2D}}{3} \quad (\text{E6-10.13})$$

$$\text{Reaction 3: } \frac{r_{3C}}{-2} = \frac{r_{3B}}{-1} = \frac{r_{3F}}{2} \quad (\text{E6-10.14})$$

$$\text{Reaction 4: } \frac{r_{4A}}{-4} = \frac{r_{4C}}{-6} = \frac{r_{4E}}{5} = \frac{r_{4D}}{6} \quad (\text{E6-10.15})$$

B. *Concentrations:* For isothermal operation and no pressure drop, the concentrations are given in terms of the molar flow rates by

$$C_j = \frac{F_j}{F_T} C_{T0}$$

Next substitute for the concentration of each species in the rate laws. Writing the rate law for species A in reaction 1 in terms of the rate of formation, r_{1A} , and molar flow rates, F_A and F_B , we obtain

$$r_{1A} = -k_{1A} C_A C_B^2 = -k_{1A} \left(C_{T0} \frac{F_A}{F_T} \right) \left(C_{T0} \frac{F_B}{F_T} \right)^2$$

Thus

$$r_{1A} = -k_{1A} C_{T0}^3 \frac{F_A F_B^2}{F_T^3} \quad (\text{E6-10.16})$$

Similarly for the other reactions,

$$r_{2A} = -k_{2A} C_{T0}^2 \frac{F_A F_B}{F_T^2} \quad (\text{E6-10.17})$$

$$r_{3B} = -k_{3B} C_{T0}^3 \frac{F_C^2 F_B}{F_T^3} \quad (\text{E6-10.18})$$

$$r_{4C} = -k_{4C} C_{T0}^{5/3} \frac{F_C F_A^{2/3}}{F_T^{5/3}} \quad (\text{E6-10.19})$$

Next, we determine the *net* rate of reaction for each species by using the appropriate stoichiometric coefficients and then summing the rates of the individual reactions.

Net rates of formation:

$$\text{Species A: } r_A = r_{1A} + r_{2A} + \frac{2}{3} r_{4C} \quad (\text{E6-10.20})$$

$$\text{Species B: } r_B = 1.25 r_{1A} + 0.75 r_{2A} + r_{3B} \quad (\text{E6-10.21})$$

$$\text{Species C: } r_C = -r_{1A} + 2 r_{3B} + r_{4C} \quad (\text{E6-10.22})$$

$$\text{Species D: } r_D = -1.5 r_{1A} - 1.5 r_{2A} - r_{4C} \quad (\text{E6-10.23})$$

$$\text{Species E: } r_E = -\frac{r_{2A}}{2} - \frac{5}{6} r_{4C} \quad (\text{E6-10.24})$$

$$\text{Species F: } r_F = -2 r_{3B} \quad (\text{E6-10.25})$$

Combining: Rather than combining the concentrations, rate laws, and mole balances to write everything in terms of the molar flow rate as we did in the past, it is more convenient here to write our computer solution (either Polymath or our own program) using equations for r_{1A} , F_A , and so on. Consequently, we shall write Equations (E6-10.16) through (E6-10.19) and (E6-10.5) through (E6-10.11) as individual lines and let the computer combine them to obtain a solution.

The corresponding Polymath program written for this problem is shown in Table E6-10.1 and a plot of the output is shown in Figure E6-10.1. One notes that there is a maximum in the concentration of NO (i.e., C) at approximately 1.5 dm³.

However, there is one fly in the ointment here: It may not be possible to determine the rate laws for each of the reactions. In this case, it may be necessary to work with the minimum number of reactions and hope that a rate law can be found for each reaction. That is, you need to find the number of linearly independent reactions in your reaction set. In Example 6-10, there are four reactions given [(E6-10.5) through (E6-10.8)]. However, only three of these reactions are independent, as the fourth can be formed from a linear combination of the other three. Techniques for determining the number of independent reactions are given by Aris.⁹

⁹ R. Aris, *Elementary Chemical Reactor Analysis* (Upper Saddle River, N.J.: Prentice Hall, 1969).



TABLE E6-10.1. POLYMATH PROGRAM

POLYMATH Results

Example 6-10 Calculating Concentrations as a Function of Position for NH₃ Oxidation in a PFR

Calculated values of the DEO variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	10	10
FA	10	1.504099	10	1.504099
FB	10	2.4000779	10	2.4000779
FC	0	0	1.6519497	0.6038017
FD	0	0	12.743851	12.743851
FE	0	0	3.4830019	3.4830019
FF	0	0	0.9260955	0.9260955
FT	20	20	21.660927	21.660927
r1A	-5	-5	-0.0341001	-0.0341001
r2A	-2	-2	-0.0615514	-0.0615514
r4C	0	-0.5619376	0	-0.0747591
r3B	0	-0.1448551	0	-0.0068877
CA	1	0.1388767	1	0.1388767
rA	-7	-7	-0.1454909	-0.1454909
rB	-7.75	-7.75	-0.0956764	-0.0956764
rC	5	-0.2008343	5	-0.0544343
rD	10.5	0.2182363	10.5	0.2182363
rE	1	0.0930749	1.0317775	0.0930749
rF	0	0	0.2897102	0.0137754

ODE Report (RK45)

Differential equations as entered by the user

- [1] d(FA)/d(V) = rA
- [2] d(FB)/d(V) = rB
- [3] d(FC)/d(V) = rC
- [4] d(FD)/d(V) = rD
- [5] d(FE)/d(V) = rE
- [6] d(FF)/d(V) = rF

Explicit equations as entered by the user

- [1] FI = FA+FB+FC+FD+FE+FF
- [2] r1A = -5*B*(FA/FI)*(FB/FI)^2
- [3] r2A = -2*A*(FA/FI)*(FB/FI)
- [4] r4C = -5*3.175*(FC/FI)*(FA/FI)^(2/3)
- [5] r3B = -10*B*(FC/FI)^2*(FB/FI)
- [6] CA = 2*FA/FI
- [7] rA = r1A+r2A+2*r4C/3
- [8] rB = 1.25*r1A+0.75*r2A+r3B
- [9] rC = -r1A+2*r3B+r4C
- [10] rD = -1.5*r1A-1.5*r2A-r4C
- [11] rE = -5*r2A-5*r4C/6
- [12] rF = -2*r3B

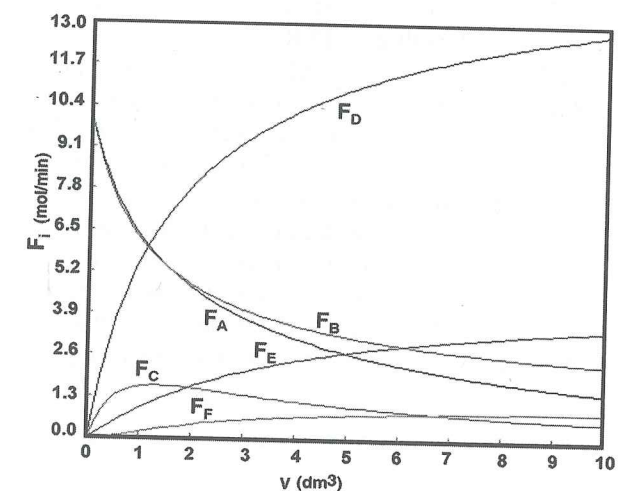


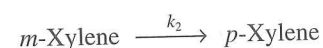
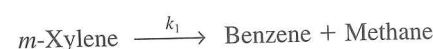
Figure E6-10.1 Molar flow rates profiles.

Sketch the trends or results you expect before working out the details of the problem.

The concentrations measured *inside* the reactor were $C_A = 0.10$, $C_B = 0.93$, $C_C = 0.51$, and $C_D = 0.049$ all in mol/dm^3 .

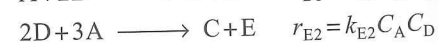
- What are r_{1A} , r_{2A} , and r_{3A} ? ($r_{1A} = -0.7 \text{ mol/dm}^3 \cdot \text{min}$)
- What are r_{1B} , r_{2B} , and r_{3B} ?
- What are r_{1C} , r_{2C} , and r_{3C} ? ($r_{1C} = 0.23 \text{ mol/dm}^3 \cdot \text{min}$)
- What are r_{1D} , r_{2D} , and r_{3D} ?
- What are r_{1E} , r_{2E} , and r_{3E} ?
- What are the net rates of formation of A, B, C, D, and E?
- The entering volumetric flow rate is $100 \text{ dm}^3/\text{min}$ and, the entering concentration of A is 3 M . What is the CSTR reactor volume? (Ans.: 4000 dm^3 .)
- Write a Polymath program to calculate the exit concentrations when the volume is given as 600 dm^3 .
- PFR.** Now assume the reactions take place in the gas phase. Use the preceding data to plot the molar flow rates as a function of PFR volume. The pressure drop parameter is 0.001 dm^{-3} , the total concentration entering the reactor is 0.2 mol/dm^3 , and $v_0 = 100 \text{ dm}^3/\text{min}$. What are $\bar{S}_{D/E}$ and $\bar{S}_{C/D}$?
- Membrane Reactor.** Repeat (i) when species C diffuses out of membrane reactor and the transport coefficient, k_C , is 10 min^{-1} . Compare your results with part (i).

P6-13_B Calculating the space time for parallel reactions. *m*-Xylene is reacted over a ZSM-5 zeolite catalyst. The following *parallel* elementary reactions were found to occur [*Ind. Eng. Chem. Res.*, 27, 942 (1988)]:



- Calculate the PFR volume to achieve 85% conversion of *m*-xylene in a packed-bed reactor. Plot the overall selectivity and yields as a function of τ . The specific reaction rates are $k_1 = 0.22 \text{ s}^{-1}$ and $k_2 = 0.71 \text{ s}^{-1}$ at 673°C . A mixture of 75% *m*-xylene and 25% inerts is fed to a tubular reactor at volumetric flow rate of $200 \text{ dm}^3/\text{s}$ and a total concentration of 0.05 mol/dm^3 . As a first approximation, neglect any other reactions such as the reverse reactions and isomerization to *o*-xylene.
- Suppose that $E_1 = 20,000 \text{ cal/mol}$ and $E_2 = 10,000 \text{ cal/mol}$, what temperature would you recommend to maximize the formation of *p*-xylene in a 2000-dm^3 CSTR?

P6-14_B The following reactions are carried out isothermally in a 50 dm^3 PFR:



Additional information: Liquid phase

$$k_{D1} = 0.25 \text{ dm}^6/\text{mol}^2 \cdot \text{min} \quad v_0 = 10 \text{ dm}^3/\text{min}$$

$$k_{E2} = 0.1 \text{ dm}^3/\text{mol} \cdot \text{min} \quad C_{A0} = 1.5 \text{ mol/dm}^3$$

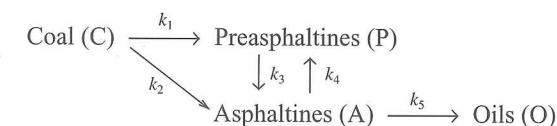
$$k_{F3} = 5.0 \text{ dm}^6/\text{mol}^2 \cdot \text{min} \quad C_{B0} = 2.0 \text{ mol/dm}^3$$

- Plot the species concentrations and the conversion of A as a function of the distance (i.e., volume) down a 50-dm^3 PFR. Note any maxima.
- Determine the effluent concentrations and conversion from a 50-dm^3 CSTR. (Ans.: $C_A = 0.61$, $C_B = 0.79$, $C_F = 0.25$, and $C_D = 0.45 \text{ mol/dm}^3$.)
- Plot the species concentrations and the conversion of A as a function of time when the reaction is carried out in a semibatch reactor initially containing 40 dm^3 of liquid. Consider two cases: (1) A is fed to B, and (2) B is fed to A. What differences do you observe for these two cases?
- Vary the ratio of B to A ($1 < \Theta_B < 10$) in the feed to the PFR and describe what you find. What generalizations can you make from this problem?
- Rework this problem for the case when the reaction is a gas-phase reaction. We will keep the constants the same so you won't have to make too many changes in your Polymath program, but we will make $v_0 = 100 \text{ dm}^3/\text{min}$, $C_{T0} = 0.4 \text{ mol/dm}^3$, $V = 500 \text{ dm}^3$ and equal molar feed of A and B. Plot the molar flow rates and \bar{S}_{CD} and \bar{S}_{EF} down a PFR.
- Repeat (e) when D diffuses out through the sides of a membrane reactor where the mass transfer coefficient, k_{CD} , can be varied between 0.1 min^{-1} and 10 min^{-1} . What trends do you find?
- Repeat (e) when B is fed through the sides of a membrane reactor.

P6-15_B Review the oxidation of formaldehyde to formic acid reactions over a vanadium titanium oxide catalyst [*Ind. Eng. Chem. Res.*, 28, 387 (1989)] shown in the ODE solver algorithm in the Summary Notes on the CD-ROM.

- Plot the species concentrations as a function of distance down the PFR for an entering flow rate of $100 \text{ dm}^3/\text{min}$ at 5 atm and 140°C . The feed is 66.7% HCHO and 33.3% O_2 . Note any maximum in species concentrations.
- Plot the yield of overall HCOOH yield and overall selectivity of HCOH to CO, of HCOOCH_3 to CH_3OH and of HCOOH to HCOOCH_3 as a function of the Θ_{O_2} . Suggest some conditions to best produce formic acid. Write a paragraph describing what you find.
- Compare your plot in part (a) with a similar plot when pressure drop is taken into account with $\alpha = 0.002 \text{ dm}^{-3}$.
- Suppose that $E_1 = 10,000 \text{ cal/mol}$, $E_2 = 30,000 \text{ cal/mol}$, $E_3 = 20,000 \text{ cal/mol}$, and $E_4 = 10,000 \text{ cal/mol}$, what temperature would you recommend for a 1000-dm^3 PFR?

P6-16_B The liquefaction of Kentucky Coal No. 9 was carried out in a slurry reactor [D. D. Gertenbach, R. M. Baldwin, and R. L. Bain, *Ind. Eng. Chem. Process Des. Dev.*, 21, 490 (1982)]. The coal particles, which were less than 200 mesh, were dissolved in a $\sim 250^\circ\text{C}$ vacuum cut of recycle oil saturated with hydrogen at 400°C . Consider the reaction sequence



which is a modified version of the one given by Gertenbach et al. All reactions are first order. Calculate the molar flow rate of each species as a function of space time in

- A plug-flow reactor.
- A 3-m^3 CSTR.
- What is the point of this problem?



Summary Notes