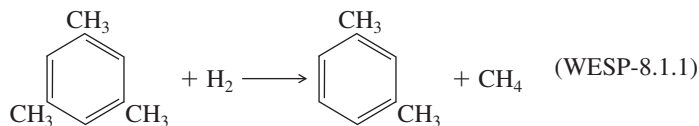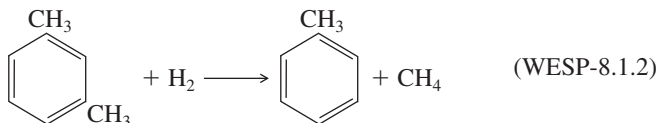**Web Solved Problems**

Web Example SP-8.1 Hydrodealkylation of Mesitylene in a PFR

The production of *m*-xylene by the hydrodealkylation of mesitylene over a Houdry Detrol catalyst[1] involves the following reactions:

$$+ \; H_2 \longrightarrow \qquad\qquad + \; CH_4 \qquad \text{(WESP-8.1.1)}$$

m-Xylene can also undergo hydrodealkylation to form toluene:

$$+ \; H_2 \longrightarrow \qquad\qquad + \; CH_4 \qquad \text{(WESP-8.1.2)}$$

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$).[2] 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,

$$-r_{1M} = k_1 C_M C_H^{0.5} \qquad \text{(WESP-8.1.3)}$$

$$r_{2T} = k_2 C_X C_H^{0.5} \qquad \text{(WESP-8.1.4)}$$

where the subscripts are: M = mesitylene, X = *m*-xylene, T = toluene, Me = methane, and H = hydrogen (H_2).

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., $k_1 = k_1' \rho_b$).
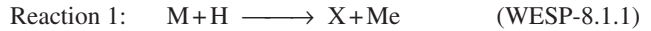
Plot the concentrations of hydrogen, mesitylene, and xylene as a function of PFR space time. Calculate the space time where the production of xylene is a maximum (i.e., τ_{opt}).

---

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

[2] 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

$$\text{Reaction 1:} \quad M+H \longrightarrow X+Me \qquad (\text{WESP-8.1.1})$$

$$\text{Reaction 2:} \quad X+H \longrightarrow T+Me \qquad (\text{WESP-8.1.2})$$

Mole balance on each and every species

1. **Mole balances:**

Hydrogen:
$$\frac{dF_H}{dV} = r_H \qquad (\text{WESP-8.1.5})$$

Mesitylene:
$$\frac{dF_M}{dV} = r_M \qquad (\text{WESP-8.1.6})$$

Xylene:
$$\frac{dF_X}{dV} = r_X \qquad (\text{WESP-8.1.7})$$

Toluene:
$$\frac{dF_T}{dV} = r_T \qquad (\text{WESP-8.1.8})$$

Methane:
$$\frac{dF_{Me}}{dV} = r_{Me} \qquad (\text{WESP-8.1.9})$$

2. **Rate laws and net rates:** Given

$$\text{Reaction 1:} \quad -r_{1M} = k_1 C_H^{1/2} C_M \qquad (\text{WESP-8.1.3})$$

$$\text{Reaction 2:} \quad r_{2T} = k_2 C_H^{1/2} C_X \qquad (\text{WESP-8.1.4})$$

Relative rates:

(1)
$$-r_{1H} = -r_{1M} = r_{1Me} = r_{1X} \qquad (\text{WESP-8.1.10})$$

(2)
$$r_{2T} = r_{2Me} = -r_{2H} = -r_{2X} \qquad (\text{WESP-8.1.11})$$

Net rates:

$$r_M = r_{1M} = -k_1 C_H^{1/2} C_M \qquad (\text{WESP-8.1.12})$$

$$r_H = r_{1H} + r_{2H} = r_{1H} - r_{2T} = -k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X \qquad (\text{WESP-8.1.13})$$

$$r_X = r_{1X} + r_{2X} = -r_{1H} - r_{2T} = k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X \qquad (\text{WESP-8.1.14})$$

$$r_{Me} = r_{1Me} + r_{2Me} = -r_{1H} + r_{2T} = k_1 C_H^{1/2} C_M + k_2 C_H^{1/2} C_X \qquad (\text{WESP-8.1.15})$$

$$r_T = r_{2T} = k_2 C_H^{1/2} C_X \qquad (\text{WESP-8.1.16})$$

3. **Stoichiometry**

The volumetric flow rate is

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

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:

$$F_H = v_0 C_H \qquad \text{(WESP-8.1.17)}$$

$$F_M = v_0 C_M \qquad \text{(WESP-8.1.18)}$$

$$F_X = v_0 C_X \qquad \text{(WESP-8.1.19)}$$

$$F_{Me} = v_0 C_{Me} = F_{H0} - F_H = v_0 (C_{H0} - C_H) \qquad \text{(WESP-8.1.20)}$$

$$F_T = F_{M0} - F_M - F_X = v_0 (C_{M0} - C_M - C_X) \qquad \text{(WESP-8.1.21)}$$

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:

$$\frac{dC_H}{d\tau} = -k_1 C_H^{1/2} C_M - k_2 C_X C_H^{1/2} \qquad \text{(WESP-8.1.22)}$$

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

$$\frac{dC_M}{d\tau} = -k_1 C_M C_H^{1/2} \qquad \text{(WESP-8.1.23)}$$

$$\frac{dC_X}{d\tau} = k_1 C_M C_H^{1/2} - k_2 C_X C_H^{1/2} \qquad \text{(WESP-8.1.24)}$$

5. **Parameter evaluation:**

At $T_0 = 1,500°$ R and $P_0 = 35$ atm, the total concentration is

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

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

$$= 0.021 \ \text{lb mol/ft}^3$$

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

$$C_{X0} = 0$$

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

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

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

We now solve these three equations, (WESP-8.1.22) to (WESP-8.1.24), simultaneously using Polymath. The program and output in graphical form are shown in Table WESP-8.1.1 and Figure WESP-8.1.1, 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.
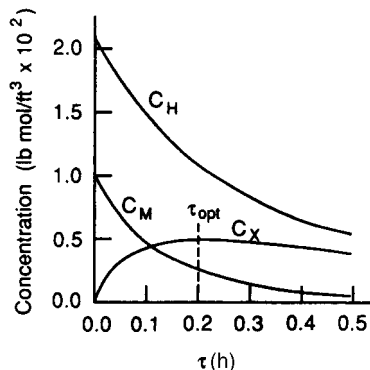

Figure WESP-8.1.1   Concentration profiles in a PFR.

TABLE WESP-8.1.1.   POLYMATH PROGRAM

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Ch)/d(tau) = r1h+r2h
[2] d(Cm)/d(tau) = r1m
[3] d(Cx)/d(tau) = r1x+r2x

Explicit equations as entered by the user
[1] k1 = 55.2
[2] k2 = 30.2
[3] r1m = -k1* Cm*(Ch^.5)
[4] r2t = k2*Cx*(Ch^.5)
[5] r1h = r1m
[6] r2m = -r2t
[7] r1x = -r1m
[8] r2x = -r2t
[9] r2h = -r2t

Living Example Problem

Web Example SP-8.2 Hydrodealkylation of Mesitylene in a CSTR

For the multiple reactions and conditions described in Web Example SP-8.1, calculate the conversion of hydrogen and mesitylene along with the exiting concentrations of mesitylene, hydrogen, and xylene in a CSTR.

Solution

As in Web Example SP-8.1, we assume $v = v_0$; for example,

$$F_A = vC_A = v_0C_A, \text{ etc.}$$

1. **CSTR Mole Balances:**

    Hydrogen: $v_0C_{H0} - v_0C_H = -r_H V$ (WESP-8.2.1)

    Mesitylene: $v_0C_{M0} - v_0C_M = -r_M V$ (WESP-8.2.2)

    Xylene: $v_0C_X = r_X V$ (WESP-8.2.3)

    Toluene: $v_0C_T = r_T V$ (WESP-8.2.4)

    Methane: $v_0C_{Me} = r_{Me} V$ (WESP-8.2.5)

2. **Net Rates**

The rate laws and net rates of reaction for these reactions were given by Equations (WESP-8.1.12) through (WESP-8.1.16) in Web Example SP-8.1.

3. **Stoichiometry:** Same as in Web Example SP-8.1.

Combining Equations (WESP-8.1.12) through (WESP-8.1.16) with Equations (WESP-8.2.11) through (WESP-8.2.3) and after dividing by v_0, ($\tau = V/v_0$), yields

$$C_{H0} - C_H = (k_1 C_H^{1/2} C_M + k_2 C_H^{1/2} C_X)\tau \qquad \text{(WESP-8.2.6)}$$

$$C_{M0} - C_M = (k_1 C_H^{1/2} C_M)\tau \qquad \text{(WESP-8.2.7)}$$

$$C_X = (k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X)\tau \qquad \text{(WESP-8.2.8)}$$

Next, we put these equations in a form such that they can be readily solved using Polymath.

$$f(C_H) = 0 = C_H - C_{H0} + (k_1 C_H^{1/2} C_M + k_2 C_H^{1/2} C_X)\tau \qquad \text{(WESP-8.2.9)}$$

$$f(C_M) = 0 = C_M - C_{M0} + k_1 C_H^{1/2} C_M \tau \qquad \text{(WESP-8.2.10)}$$

$$f(C_X) = 0 = (k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X)\tau - C_X \qquad \text{(WESP-8.2.11)}$$

The Polymath program and solution to equations (WESP-8.2.9), (WESP-8.2.10), and (WESP-8.2.1) are shown in Table WESP-8.2.1. The problem was solved for different values of τ and the results are plotted in Figure WESP-8.2.1.

For a space time of $\tau = 0.5$, the exiting concentrations are $C_H = 0.0089$, $C_M = 0.0029$, and $C_X = 0.0033$ all in lb mol/ft³. The overall conversion is

Hydrogen: $X_H = \dfrac{F_{H0} - F_H}{F_{H0}} = \dfrac{C_{H0} - C_H}{C_{H0}} = \dfrac{0.021 - 0.0089}{0.021} = 0.58$

Overall conversion

Mesitylene: $X_M = \dfrac{F_{M0} - F_M}{F_{M0}} = \dfrac{C_{M0} - C_M}{C_{M0}} = \dfrac{0.0105 - 0.0029}{0.0105} = 0.72$

TABLE WESP-8.2.1.   POLYMATH PROGRAM AND SOLUTION

NLES Solution

```
Variable        Value           f(x)          Ini Guess
Ch              0.0089436       1.995E-10      0.006
Cm              0.0029085       7.834E-12      0.0033
Cx              0.0031266      -1.839E-10      0.005
tau             0.5
```

NLES Report (safenewt)

Nonlinear equations
[1] f(Ch) = Ch-.021+(55.2*Cm*Ch^.5+30.2*Cx*Ch^.5)*tau = 0
[2] f(Cm) = Cm-.0105+(55.2*Cm*Ch^.5)*tau = 0
[3] f(Cx) = (55.2*Cm*Ch^.5-30.2*Cx*Ch^.5)*tau-Cx = 0

Explicit equations
[1] tau = 0.5

Living Example Problem

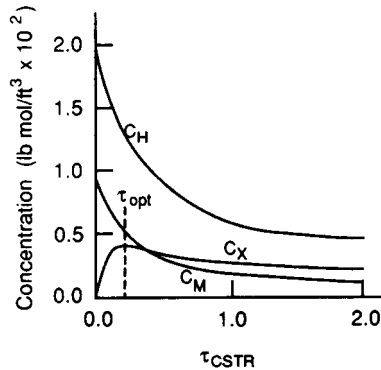To vary τ_{CSTR}, one can vary either v_0 for a fixed V or vary V for a fixed v_0.

Figure WESP-8.2.1   Concentrations as a function of space time.

We resolve Equations (WESP-8.2.6) through (WESP-8.2.11) for different values of τ to arrive at Figure WESP-8.2.1.

The moles of hydrogen consumed in reaction 1 are equal to the moles of mesitylene consumed. Therefore, the conversion of hydrogen in reaction 1 is

$$X_{1H} = \frac{C_{M0}-C_M}{C_{H0}} = \frac{0.0105-0.0029}{0.021} = X_{1H} = 0.36$$

The conversion of hydrogen in reaction 2 is just the overall conversion minus the conversion in reaction 1; that is,

$$X_{2H} = X_H - X_{1H} = 0.58 - 0.36 = 0.22$$

The yield of xylene from mesitylene based on molar flow rates exiting the CSTR for $\tau = 0.5$ is

$$\tilde{Y}_{M/X} = \frac{F_X}{F_{M0}-F_M} = \frac{C_X}{C_{M0}-C_M} = \frac{0.00313}{0.0105-0.0029}$$

$$\boxed{\tilde{Y}_{M/X} = \frac{0.41 \text{ mol xylene produced}}{\text{mole mesitylene reacted}}}$$

The overall selectivity of xylene relative to toluene is

$$\tilde{S}_{X/T} = \frac{F_X}{F_T} = \frac{C_X}{C_T} = \frac{C_X}{C_{M0}-C_M-C_X} = \frac{0.00313}{0.0105-0.0029-0.00313}$$

$$\boxed{\tilde{S}_{X/T} = \frac{0.7 \text{ mol xylene produced}}{\text{mole toluene produced}}}$$
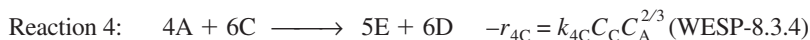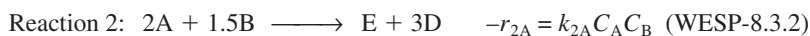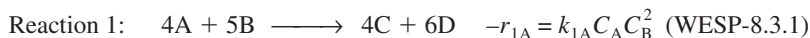
Recall that for a CSTR the overall selectivity and yield are identical with the instantaneous selectivity and yield.

Web Example SP-8.3 Calculating Concentrations as Functions of Position for NH₃ Oxidation in a PFR

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

1. $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$
2. $2NH_3 + 1.5O_2 \longrightarrow N_2 + 3H_2O$
3. $2NO + O_2 \longrightarrow 2NO_2$
4. $4NH_3 + 6NO \longrightarrow 5N_2 + 6H_2O$

Writing these equations in terms of symbols yields

Reaction 1: $4A + 5B \longrightarrow 4C + 6D$ $-r_{1A} = k_{1A}C_A C_B^2$ (WESP-8.3.1)

Reaction 2: $2A + 1.5B \longrightarrow E + 3D$ $-r_{2A} = k_{2A}C_A C_B$ (WESP-8.3.2)

Reaction 3: $2C + B \longrightarrow 2F$ $-r_{3B} = k_{3B}C_C^2 C_B$ (WESP-8.3.3)

Reaction 4: $4A + 6C \longrightarrow 5E + 6D$ $-r_{4C} = k_{4C}C_C C_A^{2/3}$ (WESP-8.3.4)

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

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

---

[3] Reaction orders and rate constants were estimated from periscosity measurements for a bulk catalyst density of 1.2 kg/dm³.

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

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

Solution

Mole balances:

Species A:
$$\frac{dF_A}{dV} = r_A \qquad \text{(WESP-8.3.5)}$$

Species B:
$$\frac{dF_B}{dV} = r_B \qquad \text{(WESP-8.3.6)}$$

Species C:
$$\frac{dF_C}{dV} = r_C \qquad \text{(WESP-8.3.7)}$$

Species D:
$$\frac{dF_D}{dV} = r_D \qquad \text{(WESP-8.3.8)}$$

Species E:
$$\frac{dF_E}{dV} = r_E \qquad \text{(WESP-8.3.9)}$$

Species F:
$$\frac{dF_F}{dV} = r_F \qquad \text{(WESP-8.3.10)}$$

Total:
$$F_T = F_A + F_B + F_C + F_D + F_E + F_F \qquad \text{(WESP-8.3.11)}$$

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

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

Stoichiometry:

    A. *Relative rates*

Reaction 1:
$$\frac{r_{1A}}{-4} = \frac{r_{1B}}{-5} = \frac{r_{1C}}{4} = \frac{r_{1D}}{6} \qquad \text{(WESP-8.3.12)}$$

Reaction 2:
$$\frac{r_{2A}}{-2} = \frac{r_{2B}}{-1.5} = \frac{r_{3E}}{1} = \frac{r_{2D}}{3} \qquad \text{(WESP-8.3.13)}$$

Reaction 3:
$$\frac{r_{3C}}{-2} = \frac{r_{3B}}{-1} = \frac{r_{3F}}{2} \qquad \text{(WESP-8.3.14)}$$

Reaction 4:
$$\frac{r_{4A}}{-4} = \frac{r_{4C}}{-6} = \frac{r_{4E}}{5} = \frac{r_{4D}}{6} \qquad \text{(WESP-8.3.15)}$$

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

$$r_{1A} = -k_1 C_A C_B^2 = -k_{1A} \left(C_{T0} \frac{F_A}{F_T} \right) \left(C_{T0} \frac{F_B}{F_T} \right)^2$$

Thus

$$r_{1A} = -k_{1A} C_{T0}^3 \frac{F_A F_B^2}{F_T^3} \qquad \text{(WESP-8.3.16)}$$

Similarly for the other reactions,

$$r_{2A} = -k_{2A} C_{T0}^2 \frac{F_A F_B}{F_T^2} \qquad \text{(WESP-8.3.17)}$$

$$r_{3B} = -k_{3B} C_{T0}^3 \frac{F_C^2 F_B}{F_T^3} \qquad \text{(WESP-8.3.18)}$$

$$r_{4C} = -k_{4C} C_{T0}^{5/3} \frac{F_C F_A^{2/3}}{F_T^{5/3}} \qquad \text{(WESP-8.3.19)}$$

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:

Species A:	$r_A = r_{1A} + r_{2A} + \frac{2}{3} r_{4C}$	(WESP-8.3.20)
Species B:	$r_B = 1.25 r_{1A} + 0.75 r_{2A} + r_{3B}$	(WESP-8.3.21)
Species C:	$r_C = -r_{1A} + 2 r_{3B} + r_{4C}$	(WESP-8.3.22)
Species D:	$r_D = -1.5 r_{1A} - 1.5 r_{2A} - r_{4C}$	(WESP-8.3.23)
Species E:	$r_E = -\frac{r_{2A}}{2} - \frac{5}{6} r_{4C}$	(WESP-8.3.24)
Species F:	$r_F = -2 r_{3B}$	(WESP-8.3.25)

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 (WESP-8.3.16) through (WESP-8.3.19) and (WESP-8.3.5) through (WESP-8.3.11) 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 WESP-8.3.1 and a plot of the output is shown in Figure WESP-8.3.1. 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 Web Example SP-8.3, there are four reactions given [(WESP-8.3.5) through (WESP-8.3.8)]. 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.[4]

_____

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

<div align="center">TABLE WESP-8.3.1.   POLYMATH PROGRAM</div>

POLYMATH Results

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

Calculated values of the DEQ 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 (RKF45)

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] Ft = FA+FB+FC+FD+FE+FF
[2] r1A = -5*8*(FA/Ft)*(FB/Ft)^2
[3] r2A = -2*4*(FA/Ft)*(FB/Ft)
[4] r4C = -5*3.175*(FC/Ft)*(FA/Ft)^(2/3)
[5] r3B = -10*8*(FC/Ft)^2*(FB/Ft)
[6] CA = 2*FA/Ft
[7] rA = r1A+r2A+2*r4C/3
[8] rB = 1.25*r1A+.75*r2A+r3B
[9] rC = -r1A+2*r3B+r4C
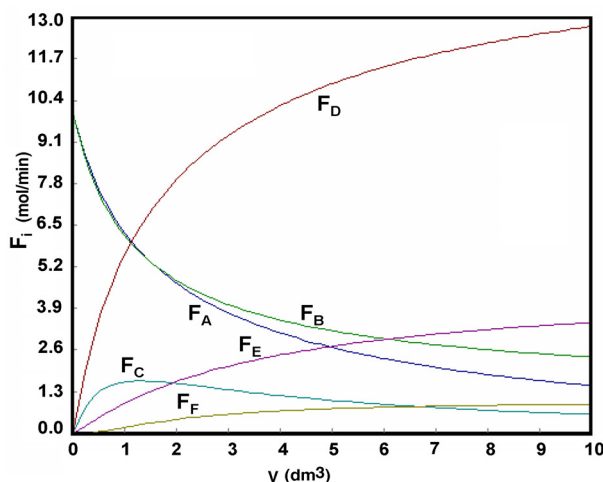[10] rD = -1.5*r1A-1.5*r2A-r4C
[11] rE = -.5*r2A-5*r4C/6
[12] rF = -2*r3B

Figure WESP-8.3.1   Molar flow rates profiles.