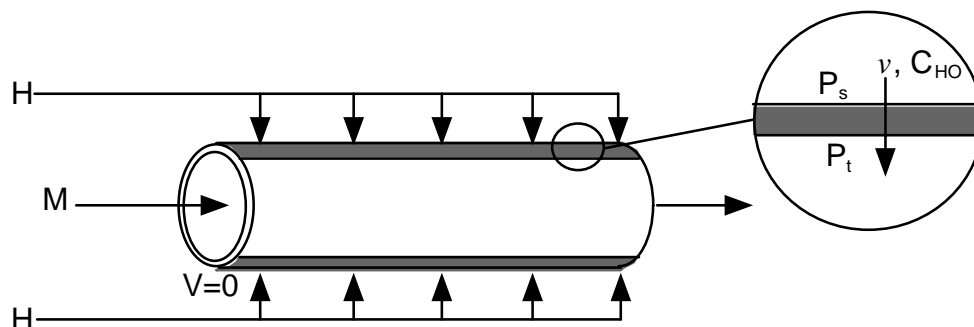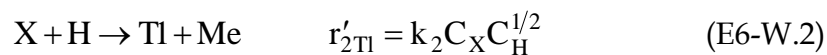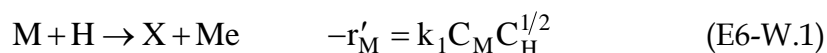## Chapter 6

CD-Solved Problems

B. Hydrodealkylation of Mesitylene in a Membrane Reactor

Now reconsider Examples 6-7 and 6-8 in which we will now use a membrane reactor and feed hydrogen uniformly through the sides of the reactor at a rate R_H, in moles hydrogen/dm^3/h. We want to compare the membrane reactor with the PFR where hydrogen was fed with mesitylene to the entrance.

The reactions and rate laws were

$$M + H \rightarrow X + Me \qquad -r'_M = k_1 C_M C_H^{1/2} \qquad \text{(E6-W.1)}$$

$$X + H \rightarrow Tl + Me \qquad r'_{2Tl} = k_2 C_X C_H^{1/2} \qquad \text{(E6-W.2)}$$

The reaction conditions and rate law of parameters are the same as described in Example 6-7. The mole fractions of mesitylene and hydrogen are to be varied, but the first run we shall choose is equal molar in hydrogen and mesitylene. Plot the molar flow rates and selectivity of xylene to toluene as a function of catalyst weight (volume) down the reactor. Compare the selectives and molar flow rates of xylene in a conventional PFR where all the hydrogen had been fed at $V = 0$ (i.e., $W = 0$).

Solution

We first apply Equation (4-44) to hydrogen.

Mole balances:

Hydrogen:
$$\frac{dF_H}{dV} = r_H + R_H \qquad \text{(E6-W.3)}$$

Mesitylene:
$$\frac{dF_M}{dV} = r_M \qquad \text{(E6-W.4)}$$

Xylene:
$$\frac{dF_X}{dV} = r_X \qquad \text{(E6-W.5)}$$

Toluene:
$$\frac{dF_{T\ell}}{dV} = r_{T\ell} \qquad\qquad \text{(E6-W.6)}$$

Methane:
$$\frac{dF_{Me}}{dV} = r_{Me} \qquad\qquad \text{(E6-W.7)}$$

Reaction rates: Recall that we have multiplied by the bulk density so that we can express the rate in per unit volume (i.e., $r_i = \rho_B r_i'$) and that $V = W/\rho_b$.

    A. Rate laws

$$-r_{1M} = k_1 C_M C_H^{1/2} \qquad\qquad \text{(E6-W.8)}$$

$$r_{2T\ell} = k_2 C_X C_H^{1/2} \qquad\qquad \text{(E6-W.9)}$$

    B. Net rates

$$r_M = r_{1M} \qquad\qquad \text{(E6-W.10)}$$

$$r_H = r_{1M} - r_{2T\ell} \qquad\qquad \text{(E6-W.11)}$$

$$r_X = r_{1M} - r_{2T\ell} \qquad\qquad \text{(E6-W.12)}$$

$$r_{T\ell} = r_{2T\ell} \qquad\qquad \text{(E6-W.13)}$$

$$r_{Me} = r_{1M} + r_{2T\ell} \qquad\qquad \text{(E6-W.14)}$$

Transport law: The rate at which hydrogen is fed through the sides of the reactor is uniform. The total volumetric flow rate across the entire membrane, v_m,

$$v_m = K[P_s - P_t]A_t \qquad\qquad \text{(E6-W.15)}$$

where K is the membrane permeability, P_s and P_t are the shell side and tube side pressures respectively, and A_t the total external surface area of the membrane (πDL). By controlling the pressure drop across the membrane, $\Delta P = (P_S - P_t)$ one can control the flow rate through the membrane.

      We recall from Equation (4-43) that "a" is the membrane surface area per unit volume of reactor

$$A_t = aV_t \qquad\qquad \text{(E6-8.16)}$$

If we were to base the rates on catalyst weight then we would use ρ_b the bulk density and express the total area as

$$A_t = \frac{a}{\rho_b} W_t$$

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If the concentration of hydrogen in the shell side C_{HS} is kept constant at the entering concentration C_{H0}, along with the pressures P_s and P, then the total molar rate of hydrogen through the sides, F_{H0} is

$$F_{H0} = \underbrace{C_{H0} \nu_m a}_{R_H} V_t \qquad \text{(E6-W.17)}$$

$$F_{H0} = R_H V_t \qquad \text{(E6-W.18)}$$

where R_H is the molar flow of hydrogen through the sides per unit volume. The amount of hydrogen that would have entered at $V = 0$ is

$$R_H = \frac{F_{H0}}{V_t} = \frac{F_{M0}\Theta_H}{V_t} = \frac{y_{H0} F_{T0}}{V_t} \qquad \text{(E6-W.19)}$$

where F_{T0} is the total molar flow rate entering and y_{H0} is the entering mole fraction of hydrogen. The total molar flow of hydrogen that has entered through the sides up the reactor to a volume V is

$$F_H = R_H V \qquad \text{(E6-W.20)}$$

Stoichiometry: For constant temperature and pressure the concentrations are

$$C_M = C_{T0}\left(\frac{F_M}{F_T}\right) \qquad \text{(E6-W.21)}$$

$$C_H = C_{T0}\left(\frac{F_H}{F_T}\right) \qquad \text{(E6-W.22)}$$

$$C_X = C_{T0}\left(\frac{F_X}{F_T}\right) \qquad \text{(E6-W.23)}$$

$$C_{T\ell} = C_{T0}\left(\frac{F_{T\ell}}{F_T}\right) \qquad \text{(E6-W.24)}$$

with $F_T = F_M + F_H + F_X + F_{Me} + F_{T\ell}$.

Recall the information from Example 6-7

$$k_1 = 55.2 \ (\text{ft}^3/\text{lb mol})^{1/2}/\text{h}, \ V_t = 238 \ \text{ft}^3, \ C_{T0} = 0.032 \frac{\text{lb mol}}{\text{ft}^3}$$

$$k_2 = 30.2 \ (\text{ft}^3/\text{lb mol})^{1/2}/\text{h}, \ \nu_0 = 476 \ \text{ft}^3/\text{hr}, \ F_{T0} = 15.2 \frac{\text{lb mol}}{\text{h}}$$

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For an equal molar feed, we have $F_{M0} = F_{H0} = 7.51$ lb mol/h. However, at the entrance to the reactor, we have $V = 0$

$$F_{M0} = 7.5 \frac{\text{lb mol}}{\text{h}}$$

$$F_{H0} = 0$$

$$R_H = \frac{F_{H0}}{V_t} = 7.5 \frac{\text{lb mol/h}}{238 \ \text{ft}^3} = 0.0316 \ \text{lb mol/h/ft}^3$$

The Polymath program and selected concentration rate profiles are shown in Table E6-W.1. If we compare the conversion and selectivity with Example 6-6, ($y_{M0} = 1/3$), we note that the membrane reactor gives an exit molar flow rate for xylene of $F_X = 2.1$ mol/h and a selectivity of $S_{X/T} = 0.89$ while the conventional reactor gives an exit flow rate of $F_X = 1.72$ mol/h and a selectivity of only $S_{X/T} = 0.58$.

TABLE E6-W.1 POLYMATH RESULTS

ODE Report (RKF45)

Differential equations as entered by the user
[1] d(Fm)/d(V) = rm
[2] d(Fh)/d(V) = rh+Rh
[3] d(Fx)/d(V) = rx
[4] d(Fme)/d(V) = rme
[5] d(Ft)/d(V) = rt

Explicit equations as entered by the user
[1] k1 = 55.2
[2] k2 = 30.2
[3] FT = Fm+Fh+Fx+Fme+Ft
[4] Cto = 0.032
[5] Ch = Cto*(Fh/FT)
[6] Cx = Cto*(Fx/FT)
[7] Cm = Cto*(Fm/FT)
[8] r1m = -k1*Cm*Ch^0.5
[9] r2t = k2*Cx*Ch^0.5
[10] rm = r1m
[11] rh = r1m-r2t
[12] rt = r2t
[13] Ct = Cto*(Ft/FT)
[14] Fbo = 7.5
[15] Vt = 238
[16] Rh = Fbo/Vt
[17] rx = -r1m-r2t
[18] rme = -r1m+r2t
[19] Cme = Cto*(Fme/FT)
[20] Sxt = Fx/(Ft+.0000000000001)
[21] vo = 476
[22] Tau = V/vo

Independent variable
variable name : V
initial value : 0

final value : 238

POLYMATH Results
No Title   12-29-2003, Rev5.1.225

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
V	0	0	238	238
Fm	7.5	2.454237	7.5	2.454237
Fh	0	0	0.9769779	0.9769779
Fx	0	0	3.5685038	3.5685038
Fme	0	0	6.5230221	6.5230221
Ft	0	0	1.4772591	1.4772591
k1	55.2	55.2	55.2	55.2
k2	30.2	30.2	30.2	30.2
FT	7.5	7.5	15	15
Cto	0.032	0.032	0.032	0.032
Ch	0	0	0.0020842	0.0020842
Cx	0	0	0.0079443	0.0076128
Cm	0.032	0.0052357	0.032	0.0052357
r1m	0	-0.028932	0	-0.0131943
r2t	0	0	0.010496	0.010496
rm	0	-0.028932	0	-0.0131943
rh	0	-0.030016	0	-0.0236903
rt	0	0	0.010496	0.010496
Ct	0	0	0.0031515	0.0031515
Fbo	7.5	7.5	7.5	7.5
Vt	238	238	238	238
Rh	0.0315126	0.0315126	0.0315126	0.0315126
rx	0	0	0.0281515	0.0026983
rme	0	0	0.030016	0.0236903
Cme	0	0	0.0139158	0.0139158
Sxt	0	0	2713.0535	2.4156248
vo	476	476	476	476
Tau	0	0	0.5	0.5

One can carry out other values of V_T and y_{H0} and this task is given as Problem 6-25. The concentration profile and the selectivity profiles are shown in

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Figure E6-W.1. Be sure to compare these profiles with those given in Example 6-7.
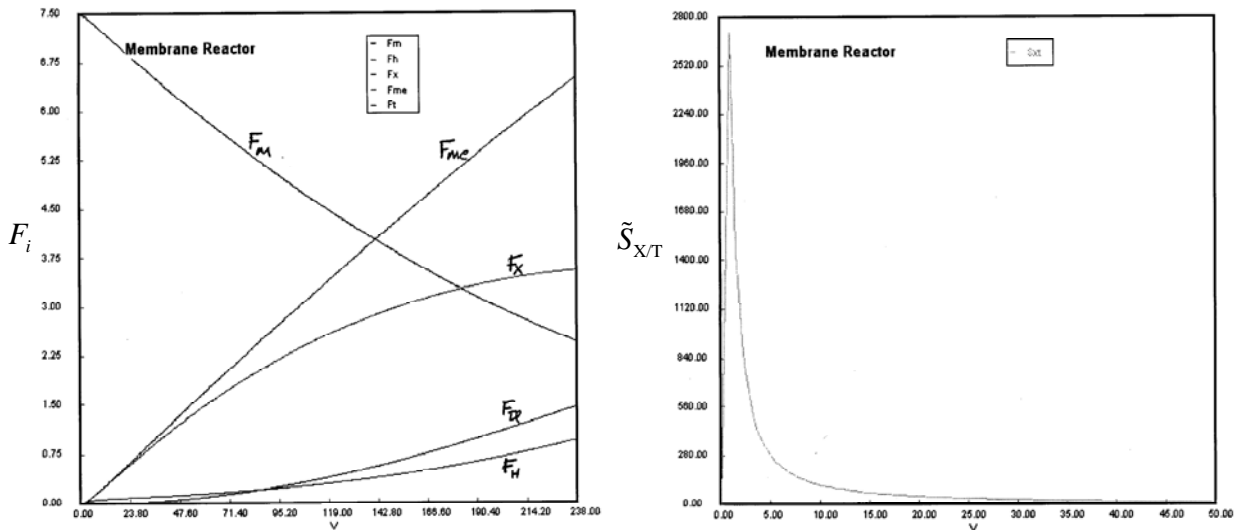

Figure E6-W.1 (a) Molar flow rate profiles; (b) Selectivity $S_{X/T}$ profiles.

From the profiles we note there is a maximum in the selectivity. Consequently, it is of interest to explore the selectivity and yield as a function of reactor length and entering feed composition. Figure E6-W.2 shows selectivity as a function of volume for two feed compositions, $y_{H0} = \frac{1}{3}$ ($F_{H0} = \frac{1}{2}F_{M0}$) and $y_{H0} = \frac{1}{2}$, ($F_{H0} = F_{M0}$). One notes a significantly higher selectivity at lower reactor volumes and lower hydrogen concentrations. Also shown on the plot are the results for a conventional PFR for the same conditions
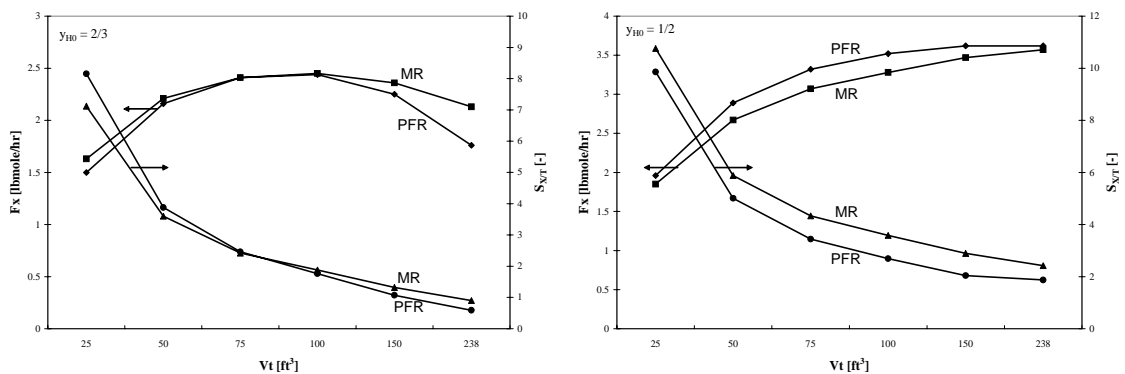

Figure E6-W.2 Selectivity and xylene molar flow rate profile. (a) $y_{H0} = \frac{2}{3}$; (b) $y_{H0} = \frac{1}{2}$

We see that, under some conditions, the membrane reactor is better than the conventional PFR but that, under other conditions, it is not. For example, for an entering mole fraction of hydrogen of $y_{H0} = 0.67$, the selectivity $S_{X/T}$ and the

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xylene molar flow rate F_X in the MR are marginally better than the PFR. While for y_{H0} = 0.5, the selectivity of the MR is better than the PFR, but for the xylene molar flow rate is somewhat better for the PFR than the MR. Problem 6-25 explores this point to map out a region where each is best.

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