Example 6-2

Reactant A decomposes by three simultaneous reactions to form three products, one that is desired, B, and two that are undesired, X and Y. These gas-phase reactions, along with the appropriate rate laws, are called the Trambouze reactions (*AIChE J.* 5, 384 (1959)).

1) \[ A \xrightarrow{k_1} X \quad -r_{1A} = r_X = k_1 = 0.0001 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \]

2) \[ A \xrightarrow{k_2} B \quad -r_{2A} = r_B = k_2 C_A = (0.0015 \text{ s}^{-1}) C_A \]

3) \[ A \xrightarrow{k_3} Y \quad -r_{3A} = r_Y = k_3 C_A^2 = 0.008 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} C_A^2 \]

The specific reaction rates are given at 300 K and the activation energies for reactions (1), (2), and (3) are \( E_1 = 10,000 \text{ kcal/mole} \), \( E_2 = 15,000 \text{ kcal/mole} \), and \( E_3 = 20,000 \text{ kcal/mole} \), respectively. How and under what conditions (e.g. reactor type(s), temperature, concentrations) should the reaction be carried out to maximize the selectivity of B for an entering concentration of A of 0.4 M and a volumetric flow rate of 2 dm\(^3\)/s.
Figure E6-2.1  Selectivity as a function of the concentration of A.
Table E6-2.1. POLYMATH PROGRAM FOR PFR FOLLOWING CSTR

POLYMATH Results
Example 6-2 Maximizing the Selectivity for the Trambouze Reactions 08-12-2004, Rev5.1.232

ODE Report (RK45)
Differential equations as entered by the user
1. \[\frac{d(C_A)}{d(tau)} = -k_1 \cdot k_2 \cdot C_A \cdot k_3 \cdot C_A^2\]
2. \[\frac{d(C_B)}{d(tau)} = k_1\]
3. \[\frac{d(C_X)}{d(tau)} = k_2 \cdot C_A\]
4. \[\frac{d(C_Y)}{d(tau)} = k_3 \cdot C_A^2\]

Explicit equations as entered by the user
1. \[C_A = 0.4\]
2. \[X = 1 - C_A/C_A^0\]
3. \[k_1 = 0.0001\]
4. \[k_2 = 0.0015\]
5. \[k_3 = 0.008\]
6. \[S_{xy} = C_b/(C_x + C_y)\]

Calculated values of the DEQ variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>initial value</th>
<th>minimal value</th>
<th>maximal value</th>
<th>final value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau)</td>
<td>0</td>
<td>0</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>(C_A)</td>
<td>0.112</td>
<td>0.0376588</td>
<td>0.112</td>
<td>0.0376588</td>
</tr>
<tr>
<td>(C_B)</td>
<td>0.0783</td>
<td>0.0783</td>
<td>0.1083</td>
<td>0.1083</td>
</tr>
<tr>
<td>(C_X)</td>
<td>0.132</td>
<td>0.132</td>
<td>0.1634944</td>
<td>0.1634944</td>
</tr>
<tr>
<td>(C_Y)</td>
<td>0.0786</td>
<td>0.0786</td>
<td>0.0914368</td>
<td>0.0914368</td>
</tr>
<tr>
<td>(C_{ao})</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
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<tr>
<td>(X)</td>
<td>0.72</td>
<td>0.72</td>
<td>0.905828</td>
<td>0.905828</td>
</tr>
<tr>
<td>(k_1)</td>
<td>1.08E-04</td>
<td>1.08E-04</td>
<td>1.08E-04</td>
<td>1.08E-04</td>
</tr>
<tr>
<td>(k_2)</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0015</td>
<td>0.0015</td>
</tr>
<tr>
<td>(k_3)</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>(S_{xy})</td>
<td>0.8413002</td>
<td>0.8185493</td>
<td>0.8413002</td>
<td>0.8185493</td>
</tr>
</tbody>
</table>

Figure E6-2.2 (a) PFR concentration profiles; (b) PFR Selectivity profile.
REACTOR SELECTION AND OPERATING CONDITIONS
FOR MORE COMPLEX PARALLEL REACTIONS

\[ \text{A} + \text{B} \xrightarrow{k_1} \text{D} \quad r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1} \]

\[ \text{A} + \text{B} \xrightarrow{k_2} \text{U} \quad r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2} \]

**CASE 1:** \( \alpha_1 > \alpha_2 \) and \( \beta_1 > \beta_2 \)

\[
S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^a C_B^b
\]

where: \( a = \alpha_1 - \alpha_2 \) and \( b = \beta_1 - \beta_2 \)

**CASE 2:** \( \alpha_1 > \alpha_2 \) and \( \beta_2 > \beta_1 \)

\[
S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} \frac{C_A^a}{C_B^b}
\]

where: \( a = \alpha_1 - \alpha_2 \) and \( b = \beta_1 - \beta_2 \)
**CASE 3:** \( \alpha_2 > \alpha_1 \) and \( \beta_2 > \beta_1 \)

\[
S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2 C_A^a C_B^b}
\]

where: \( a=\alpha_1-\alpha_2 \) and \( b=\beta_1-\beta_2 \)

**CASE 4:** \( \alpha_2 > \alpha_1 \) and \( \beta_1 > \beta_2 \)

\[
S_{D/U} = \frac{r_D}{r_U} = \frac{k_1 C_B^b}{k_2 C_A^a}
\]

where: \( a=\alpha_1-\alpha_2 \) and \( b=\beta_1-\beta_2 \)
MAXIMIZING THE DESIRED PRODUCT IN SERIES REACTIONS

\[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \]

Assumptions:
- Isothermal batch reactor
- Volume: \( V = V_0 = \text{const} \)
- Isothermal PFR reactor
- Pressure drop is negligible
- Volumetric flow rate: \( v = v_0 = \text{const} \)

BATCH OR PFR REACTOR

Mole balances on A and B:

\[
\frac{dN_A}{dt} = r_A V \quad \text{or} \quad \frac{dF_A}{dV} = r_A
\]

\[
\frac{dN_B}{dt} = r_B V \quad \text{or} \quad \frac{dF_B}{dV} = r_B
\]

Rate laws

\[
r_A = -k_1 C_A \quad \text{and} \quad r_B = k_1 C_A - k_2 C_B
\]
\[
\frac{dC_A}{d\tau} = -k_1 C_A \\
C_A = C_{A0} e^{-k_1 \tau}
\]
\[
\frac{dC_B}{d\tau} = k_1 C_A - k_2 C_B \\
C_B = k_1 C_{A0} \left( \frac{e^{-k_1 \tau} - e^{-k_2 \tau}}{k_2 - k_1} \right)
\]

**OPTIMUM YIELD**

\[
\frac{dC_B}{d\tau} = 0 = \frac{k_1 C_{A0}}{k_2 - k_1} \left[ -k_1 e^{-k_1 \tau} + k_2 e^{-k_2 \tau} \right]
\]
\[
\tau_{opt} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}
\]
\[
X_{opt} = \frac{C_{A0} - C_A}{C_{A0}} = 1 - e^{-k_1 \tau_{opt}}
\]
CSTR REACTOR

Class Problem

Derive equations for calculations of optimum space time, $\tau$, for the reaction $A \rightarrow B \rightarrow C$ with known $k_1$ and $k_2$, which maximize concentration of $B$ at the exit from a single CSTR. The reactor operates under isothermal conditions with $v=v_0$. The pressure drop across the reactor can be neglected.