

16. Appendix E.

Governing equations (8.25) and boundary conditions (8.21e) still involve the reactant profiles explicitly. Thus, to track evolution of the profile moments and consequently determine the final selectivity, one should define functions approximating the reactant concentration profiles in the interval $0 \leq \xi \leq 1$. In this case, two parameter functions were used to approximate the real concentration profiles. Some of them were identical with those proposed by Tryggvason and Dahm [74], other were very similar.

The first concentration profile of reactant A, sketched in figure E.1a, is defined as:

$$C_A(\xi, \tau) = \begin{cases} 1 & 0 \leq \xi \leq \Delta_A - \delta_A/2 \\ 0.5 - (\xi - \Delta_A)/\delta_A & \Delta_A - \delta_A/2 < \xi < \Delta_A + \delta_A/2 \\ 0 & \Delta_A + \delta_A/2 \leq \xi \leq 1 \end{cases}, \quad (\text{E.1a})$$

where Δ_A is the displacement of the reactant gradient profile from the coordinate origin and δ_A is its width. According to expressions (8.23) and (8.24a) the first moment for this profile becomes:

$$M_1^A = -\Delta_A \quad (\text{E.1b})$$

and equation (8.25a) takes form:

$$-\frac{d\Delta_A}{d\tau} = \frac{1}{\delta_A} + Da \cdot \left(\frac{s}{s_0}\right)^2 \cdot \int_0^{\Delta_A + \delta_A/2} C_A \cdot C_C d\xi. \quad (\text{E.1c})$$

If only the reactant gradient profile (E.1a) approaches the coordinate origin ($\Delta_A - \delta_A/2 = 0$), another approximation should be used (see figure E.1b):

$$C_A(\xi, \tau) = \begin{cases} C_{AM} \cdot (1 - \xi/\delta_A) & 0 \leq \xi < \delta_A \\ 0 & \delta_A \leq \xi \leq 1 \end{cases}, \quad (\text{E.2a})$$

which results in

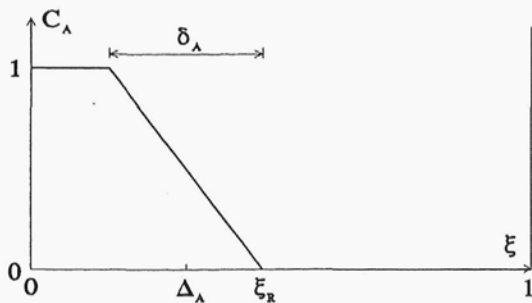


Figure E.1a. Reagent A - first profile.

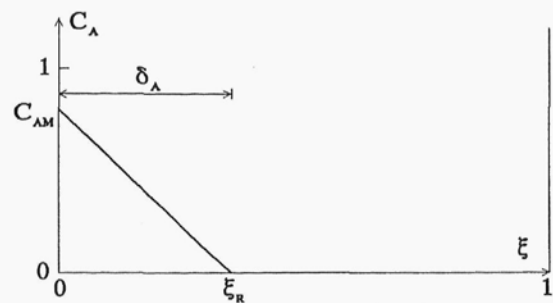


Figure E.1b. Reagent A - second profile.

$$M_1^A = -C_{AM} \cdot \delta_A / 2 \quad (\text{E.2b})$$

$$-\frac{1}{2} \cdot \frac{d(C_{AM} \cdot \delta_A)}{d\tau} = \frac{C_{AM}}{\delta_A} + Da \cdot \left(\frac{s}{s_0} \right)^2 \cdot \int_0^{\delta_A} C_A \cdot C_C d\xi . \quad (\text{E.2c})$$

Similarly, the first profile of reactant B, sketched in figure E.2a can be defined as:

$$C_B(\xi, \tau) = \begin{cases} 0 & 0 \leq \xi \leq \Delta_B - \delta_B / 2 \\ (c_{B0}/c_{A0}) \cdot [0.5 + (\xi - \Delta_B)/\delta_B] & \Delta_B - \delta_B / 2 < \xi < \Delta_B + \delta_B / 2 \\ c_{B0}/c_{A0} & \Delta_B + \delta_B / 2 \leq \xi \leq 1 \end{cases} \quad (\text{E.3a})$$

In this case, one receives from expressions (8.23), (8.24b) and (8.25b) as follows:

$$M_B^1 = \frac{c_{B0}}{c_{A0}} \cdot \Delta_B , \quad (\text{E.3b}) \quad \frac{d\Delta_B}{d\tau} = \frac{D_B}{D_A} \cdot \frac{1}{\delta_B} . \quad (\text{E.3c})$$

The second approximation (figure E.2b) should be used when the reactant gradient profile approaches right border of the computational domain ($\Delta_B + \delta_B / 2 = 1$):

$$C_B(\xi, \tau) = \begin{cases} 0 & 0 \leq \xi \leq 1 - \delta_B \\ (c_{B0}/c_{A0}) \cdot [1 + (\xi - 1)/\delta_B] \cdot C_{BM} & 1 - \delta_B < \xi \leq 1 \end{cases} , \quad (\text{E.4a})$$

which yields:

$$M_B^1 = \frac{c_{B0}}{c_{A0}} \cdot \left(1 - \frac{\delta_B}{2} \right) \cdot C_{BM} , \quad (\text{E.4b}) \quad \frac{d}{d\tau} \left[C_{BM} \cdot \left(\frac{\delta_B}{2} - 1 \right) \right] = \frac{D_B}{D_A} \cdot \frac{C_{BM}}{\delta_B} + \frac{dC_{BM}}{d\tau} . \quad (\text{E.4c})$$

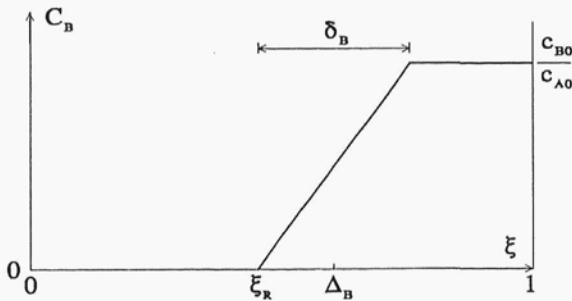


Figure E.2a. Reagent B - first profile.

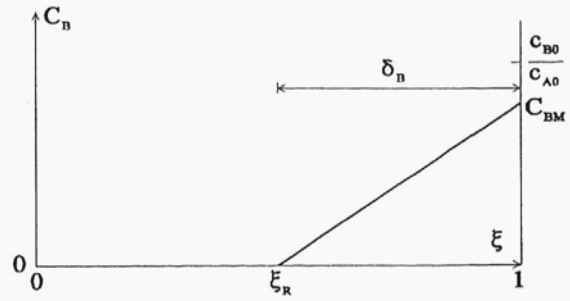


Figure E.2b. Reactant B - second profile.

Concentration profiles (E.1a), (E.2a), (E.3a) and (E.4a) have to fulfil boundary condition (8.21e). Table E.I shows four possible pairs of relationships arising from this condition.

Table E.I. Pairs of equations arising from boundary condition (8.21e).

Reactant profiles		$C_A = C_B = 0$	$(\partial C_A / \partial \xi) + D_B / D_A \cdot (\partial C_B / \partial \xi) = 0$
A	B		
(E.1a)	(E.3a)	$\Delta_A + \delta_A / 2 = \Delta_B - \delta_B / 2$	$1 / \delta_A = (c_{B0} / c_{A0}) \cdot (D_B / D_A) / \delta_B$
(E.1a)	(E.4a)	$\Delta_A + \delta_A / 2 = 1 - \delta_B$	$1 / \delta_A = (c_{B0} / c_{A0}) \cdot (D_B / D_A) \cdot C_{BM} / \delta_B$
(E.2a)	(E.3a)	$\delta_A = \Delta_B - \delta_B / 2$	$C_{AM} / \delta_A = (c_{B0} / c_{A0}) \cdot (D_B / D_A) / \delta_B$
(E.2a)	(E.4a)	$\delta_A = 1 - \delta_B$	$C_{AM} / \delta_A = (c_{B0} / c_{A0}) \cdot (D_B / D_A) \cdot C_{BM} / \delta_B$

Four relationships were used to approximate the real concentration profile of reactant C. The first profile, sketched in figure E.3a, is defined as:

$$C_C(\xi, \tau) = \begin{cases} 0 & 0 \leq \xi \leq \Delta_C - \delta_C / 2 \\ (c_{C0} / c_{A0}) \cdot [0.5 + (\xi - \Delta_C) / \delta_C] & \Delta_C - \delta_C / 2 < \xi < \Delta_C + \delta_C / 2 \\ c_{C0} / c_{A0} & \Delta_C + \delta_C / 2 \leq \xi \leq 1 \end{cases} \quad (\text{E.5a})$$

Thus, expressions (8.23) for $j=1$ and (8.25c) read:

$$M_C^1 = \frac{c_{C0}}{c_{A0}} \cdot \Delta_C, \quad (\text{E.5b}) \quad \frac{d\Delta_C}{d\tau} = Da \cdot \left(\frac{s}{s_0} \right)^2 \cdot \int_{\Delta_C - \delta_C / 2}^1 C_A \cdot C_C d\xi, \quad (\text{E.5c})$$

whereas expressions (8.23) for $j=2$ and (8.25d) become:

$$M_C^2 = \frac{c_{C0}}{c_{A0}} \cdot \left(\Delta_C^2 + \frac{\delta_C^2}{12} \right), \quad (\text{E.5d})$$

$$\frac{d}{d\tau} \left(\Delta_C^2 + \frac{\delta_C^2}{12} \right) = 2 \cdot \frac{D_C}{D_A} + 2 \cdot Da \cdot \left(\frac{s}{s_0} \right)^2 \cdot \int_{\Delta_C - \delta_C / 2}^1 C_A \cdot C_C \cdot \xi d\xi. \quad (\text{E.5e})$$

Profile (E.5a) should be replaced by the second profile, shown in figure E.3b, when $\Delta_C + \delta_C / 2 \geq 1$:

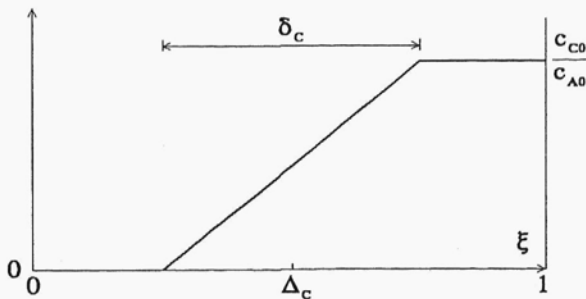


Figure E.3a. Reagent C - first profile.

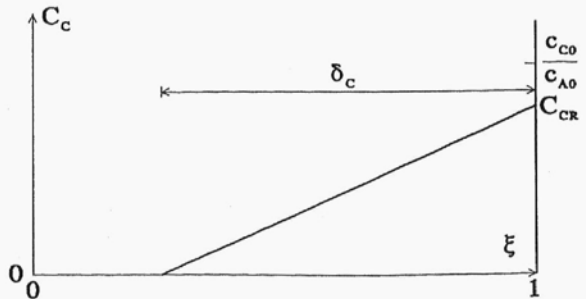


Figure E.3b. Reagent C - second profile.

$$C_C(\xi, \tau) = \begin{cases} 0 & 0 \leq \xi \leq 1 - \delta_C \\ (c_{C0}/c_{A0}) \cdot [1 + (\xi - 1)/\delta_C] \cdot C_{CR} & 1 - \delta_C < \xi \leq 1 \end{cases} \quad (\text{E.6a})$$

Application of approximation (E.6b) in expressions (8.23), (8.25c) and (8.25d) results in:

$$M_C^1 = \frac{c_{C0}}{c_{A0}} \cdot \left(1 - \frac{\delta_C}{2}\right) \cdot C_{CR} \quad (\text{E.6b})$$

$$\frac{d}{d\tau} \left[C_{CR} \cdot \left(\frac{\delta_C}{2} - 1 \right) \right] = \frac{dC_{CR}}{d\tau} + Da \cdot \left(\frac{s}{s_0} \right)^2 \cdot \int_{1-\delta_C}^1 C_A \cdot C_C d\xi \quad (\text{E.6c})$$

and

$$M_C^2 = \frac{c_{C0}}{c_{A0}} \cdot \left(1 - \delta_C + \frac{\delta_C^2}{3}\right) \cdot C_{CR} \quad (\text{E.6d})$$

$$\frac{d}{d\tau} \left[C_{CR} \cdot \left(1 - \delta_C + \frac{\delta_C^2}{3}\right) \right] = \frac{dC_{CR}}{d\tau} + 2 \cdot C_{CR} \cdot \frac{D_C}{D_A} + 2 \cdot Da \cdot \left(\frac{s}{s_0} \right)^2 \cdot \int_{1-\delta_C}^1 C_A \cdot C_C \cdot \xi d\xi \quad (\text{E.6e})$$

On the other hand, if $\Delta_C - \delta_C/2 \leq 0$ then initial profile (E.5a) should be replaced by the third profile - presented in figure E.3c:

$$C_C(\xi, \tau) = \begin{cases} (c_{C0}/c_{A0}) \cdot [C_{CL} + (1 - C_{CL}) \cdot \xi/\delta_C] & 0 \leq \xi < \delta_C \\ c_{C0}/c_{A0} & \delta_C \leq \xi \leq 1 \end{cases} \quad (\text{E.7a})$$

In this case, expressions (8.23), (8.25c) and (8.25d) can be written as follows:

$$M_C^1 = \frac{c_{C0}}{c_{A0}} \cdot \delta_C \cdot \frac{1 - C_{CL}}{2} \quad (\text{E.7b}) \quad \frac{d}{d\tau} [\delta_C \cdot (1 - C_{CL})] = 2 \cdot Da \cdot \left(\frac{s}{s_0} \right)^2 \cdot \int_0^1 C_A \cdot C_C d\xi \quad (\text{E.7c})$$

and

$$M_C^2 = \frac{c_{C0}}{c_{A0}} \cdot \delta_C^2 \cdot \frac{1 - C_{CL}}{3} \quad (\text{E.7d})$$

$$\frac{d}{d\tau} [\delta_C^2 \cdot (1 - C_{CL})] = 6 \cdot (1 - C_{CL}) \cdot \frac{D_C}{D_A} + 6 \cdot Da \cdot \left(\frac{s}{s_0} \right)^2 \cdot \int_0^1 C_A \cdot C_C \cdot \xi d\xi \quad (\text{E.7e})$$

The third profile can be again replaced by the first one when $C_{CL} \leq 0$ or by the fourth one:

$$C_C(\xi, \tau) = (c_{C0}/c_{A0}) \cdot [C_{CL} + (C_{CR} - C_{CL}) \cdot \xi] \quad 0 \leq \xi \leq 1 \quad (\text{E.8a})$$

shown in figure E.3d, if $\delta_C \geq 1$. Thus, expressions (8.23), (8.25c) and (8.25d) become:

$$M_C^1 = \frac{c_{C0}}{c_{A0}} \cdot \frac{C_{CR} - C_{CL}}{2} , \quad (E.8b)$$

$$\frac{d}{d\tau}(C_{CR} - C_{CL}) = 2 \cdot \frac{dC_{CR}}{d\tau} + 2 \cdot Da \cdot \left(\frac{s}{s_0}\right)^2 \cdot \int_0^1 C_A \cdot C_C d\xi \quad (E.8c)$$

and

$$M_C^2 = \frac{c_{C0}}{c_{A0}} \cdot \frac{C_{CR} - C_{CL}}{3} , \quad (E.8d)$$

$$\frac{d}{d\tau}(C_{CR} - C_{CL}) = 3 \cdot \frac{dC_{CR}}{d\tau} + 6 \cdot (C_{CR} - C_{CL}) \cdot \frac{D_C}{D_A} + 6 \cdot Da \cdot \left(\frac{s}{s_0}\right)^2 \cdot \int_0^1 C_A \cdot C_C \cdot \xi d\xi . \quad (E.8e)$$

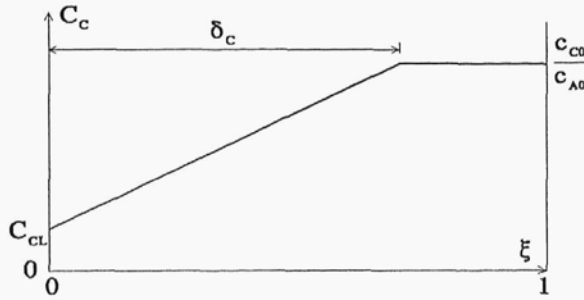


Figure E.3c. Reagent C - third profile.

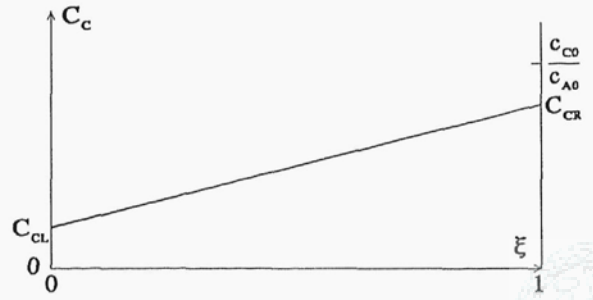


Figure E.3d. Reagent C - fourth profile.

The fourth profile can be replaced by the second one if $C_{CL} \leq 0$ and vice versa when $\delta_C \geq 1$ then the second profile should be replaced by the fourth one.

Initial conditions (8.21f) and (8.21g) can be fulfilled only by approximations (E.1a), (E.3a) and (E.5a); for $\tau=0$ the profile parameters are equal to:

$$\Delta_A = \Delta_B = \Delta_C = \delta_0 / (2 \cdot s_0) \quad \text{and} \quad \delta_A = \delta_B = \delta_C = 0 . \quad (E.9)$$

Application of the backward Euler scheme to the system of four differential equations (E.1c), (E.3c), (E.5c) and (E.5e) and two algebraic equations from the first row in table E.I gives the system of six nonlinear algebraic equations, which can be solved at each time step using either successive substitution or Newton-Raphson method. After each time step, one has to check if is necessary to replace one approximation of the reactant concentration profile with another and consequently modify the governing equations.