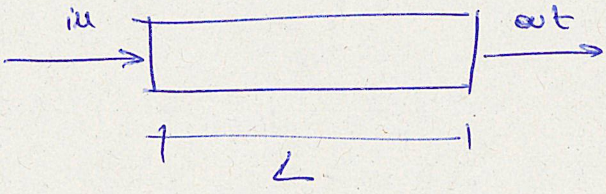
PRACTICAL SESSION 1

EXERCISE 1 : isothermal plug flow reactor



$L = 100\ m$

$d = 0.08\ m$

$T = 750\ °C$

$P = 3\ bar$

$\dot{F}_{tot}^{in} = 20\ kmol/h \quad \begin{cases} \dot{F}_A^{in} = 20\ kmol/h \\ \dot{F}_B^{in} = 0 \\ \dot{F}_C^{in} = 0 \end{cases}$

$MW_A = MW_B = MW_C = 25\ g/mol$

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\begin{cases} r_1 = k_1 C_A \\ r_2 = k_2 C_B \end{cases} \quad \text{reaction rates}$$

$$\begin{cases} R_A = -r_1 \\ R_B = r_1 - r_2 \\ R_C = r_2 \end{cases} \quad \text{governing equations} \quad \begin{cases} \dfrac{d\dot{F}_A}{dV} = R_A \\ \dfrac{dF_B}{dV} = R_B \\ \dfrac{dF_C}{dV} = R_C \end{cases}$$

Hyp. : $\rho = const$

governing equations

$$\begin{cases} \dfrac{dC_A}{d\tau} = R_A \\ \dfrac{dC_B}{d\tau} = R_B \\ \dfrac{dC_C}{d\tau} = R_C \end{cases} \rightarrow \begin{cases} \dfrac{dC_A}{d\tau} = -k_1 C_A \\ \dfrac{dC_B}{d\tau} = k_1 C_A - k_2 C_B \\ \dfrac{dC_C}{d\tau} = k_2 C_B \end{cases}$$

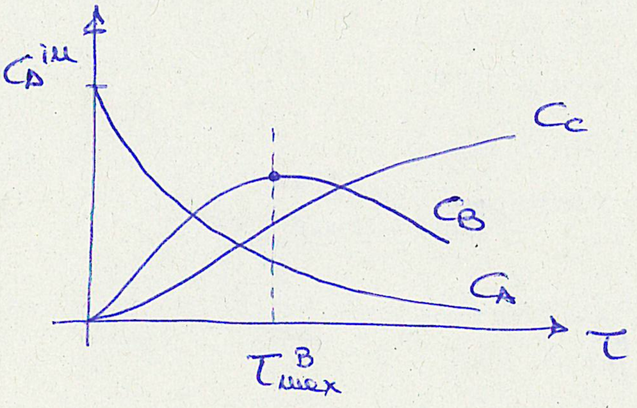
system of ODE + initial conditions (IVP)

$$\begin{cases} \dfrac{dC_A}{d\tau} = -k_1 C_A & \oplus \quad C_A(\tau=0) = C_A^{in} \\ \dfrac{dC_B}{d\tau} = k_1 C_A - k_2 C_B & \oplus \quad C_B(\tau=0) = C_B^{in} = 0 \\ \dfrac{dC_C}{d\tau} = k_2 C_B & \oplus \quad C_B(\tau=0) = C_C^{in} = 0 \end{cases}$$

Analytical solution

(see Practical session 0 exercise 6)

$$\begin{cases} C_A(\tau) = C_A^{in}\exp(-k_1\tau) \\ C_B(\tau) = \dfrac{k_1 C_A^{in}}{k_2-k_1}\left(\exp(-k_1\tau) - \exp(-k_2\tau)\right) \\ C_C(\tau) = C_A^{in} - C_A(\tau) - C_B(\tau) \end{cases}$$



yield

$$Y_C = \frac{C_C(\tau)}{C_A^{in}} = \frac{C_A^{in} - C_A(\tau) - C_B(\tau)}{C_A^{in}} =$$

$$= 1 - \exp(-k_1\tau) - \frac{k_1}{k_2-k_1}\left(\exp(-k_1\tau) - \exp(-k_2\tau\right)$$

$$Y_C(\tau) = 1 - \exp(-k_1\tau) - \frac{k_1}{k_2-k_1}\left(\exp(-k_1\tau) - \exp(-k_2\tau)\right)$$

EXERCISE 2 : parallel reactions in a batch reactor

$$\begin{cases} A \rightarrow B \\ A \rightarrow C \end{cases} \qquad \begin{cases} k_1 = 1.69 \ 1/h \\ k_2 = 0.13 \ 1/h \end{cases}$$

$\rho = 800 \ kg/m^3$
$T = 100°C$
$V = 1 \ m^3$
$\tau_D = 1 h$

Costs & Revenue

$$\begin{cases} C_F(\tau) = C_1 \tau_D + C_2 \tau + C_3 \\ \hat{I}(\tau) = 15 \ \$/kg_B \end{cases}$$

$C_1 = 100 \ \$/h$
$C_2 = 25 \ \$/h$
$C_3 = 8000 \ \$$

governing equations

$$\begin{cases} \dfrac{dC_A}{dt} = R_A \\ \dfrac{dC_B}{dt} = R_B \\ \dfrac{dC_C}{dt} = R_C \end{cases} \longrightarrow \begin{cases} \dfrac{dC_A}{dt} = -K_1 C_A - K_2 C_A \\ \dfrac{dC_B}{dt} = K_1 C_A \\ \dfrac{dC_C}{dt} = K_2 C_A \end{cases}$$

$+$

IC

analytical solution

$$\frac{dC_A}{dt} = -(K_1+K_2) C_A = -(K_{TOT} \cdot C_A)$$

where $K_{TOT} = K_1 + K_2$

$$\frac{dC_A}{dt} = -K_{tot} C_A \rightarrow \frac{dC_A}{C_A} = -K_{tot}\, dt$$

$$C_A = C_A^\circ \exp(-K_{tot}\, t)$$

$$\frac{dC_B}{dt} = +K_1 C_A = K_1 C_A^\circ \exp(-K_{tot} \cdot t)$$

$$\frac{dC_B}{dt} = K_1 C_A^\circ \cdot \exp(-K_{tot}\, t)$$

$$\int_0^{C_B} dC_B = K_1 C_A^\circ \int_0^t \exp(-K_{tot}\, t)\, dt$$

$$C_B = \frac{K_1 C_A^\circ}{K_{tot}} (1 - \exp(-K_{tot}\, t)$$

$$C_C = \frac{K_2 C_A^\circ}{K_{tot}} (1 - \exp(-K_{tot}\, t)$$

$$\longrightarrow \begin{cases} C_A(t) = C_A^\circ \exp(-K_{tot}\, t) \\ C_B(t) = \dfrac{K_1 C_A^\circ}{K_{tot}} \cdot (1 - \exp(-K_{tot}\, t)) \\ C_C(t) = \dfrac{K_2 C_A^\circ}{K_{tot}} (1 - \exp(-K_{tot}\, t)) \end{cases}$$

target conversion $\tilde{X} = 0.98 \longrightarrow$ residence time $\tau = ?$

$$C_A(t) = C_A^0 \exp(-kt) \qquad C_A(t) = C_A^0(1 - X(t))$$

$$1 - X(t) = \exp(-kt) \longrightarrow 1 - \tilde{X} = \exp(-k\tau)$$

$$-k\tau = \ln(1 - \tilde{X})$$

$$\boxed{\tau = -\frac{1}{k}\ln(1-\tilde{X})}$$

$$\tau = \dots = 2.18\,h$$

number of cycles per day (24h) $\qquad n_{cyc/day} = \dfrac{24\,h}{\tau + \tau_D} = 7.52$

production of B per day (24h) $\qquad P_B = C_B(\tau) \cdot V \cdot n_{cyc/day} =$

$$\stackrel{!}{=} \dots = 155.5\ kmol/day$$

Optimal economical conditions

$M = I - C \qquad$ MARGIN = INCOME − COSTS

↑

to be maximized

$$\hat{I} = 15\ \$/kg_B \rightarrow I = P_B \cdot \hat{I} \cdot MW_B$$

$$\stackrel{!}{=} \underbrace{\frac{24}{\tau_{opt} + \tau_D} \cdot C_B(\tau_{opt}) \cdot V}_{P_B} \cdot \hat{I} \cdot MW_B$$

$$I(\tau_{opt}) = \frac{24}{\tau_{opt}+\tau_D} \cdot V \cdot \hat{I} \cdot MW_B \cdot \frac{k_1 C_D^0}{k_{tot}} \cdot \left(1 - \exp(-k_1 \tau_{opt})\right)$$

$$\perp \quad \beta \cdot \frac{1-\exp(-k_1 \tau_{opt})}{\tau_D + \tau_{opt}}$$

where $\beta = 24 \cdot V \cdot \hat{I} \cdot MW_B \cdot \frac{k_1 C_D^0}{k_{tot}}$

Costs $C(\tau_{opt}) = \left(C_1 \cdot \tau_D + C_2 \tau_{opt} + C_3\right) \cdot n_{cyc/day}$

$$\perp \quad \frac{24}{\tau_D+\tau_{opt}} \left(C_1 \tau_D + C_2 \tau_{opt} + C_3\right)$$

Margin $M = -\text{Costs} + \text{Income} = I - C$

$$M = \frac{\beta\left(1 - \exp(-k_1 \tau_{opt})\right) - 24\left(C_1 \tau_D + C_2 \tau_{opt} + C_3\right)}{\tau_D + \tau_{opt}}$$

maximum

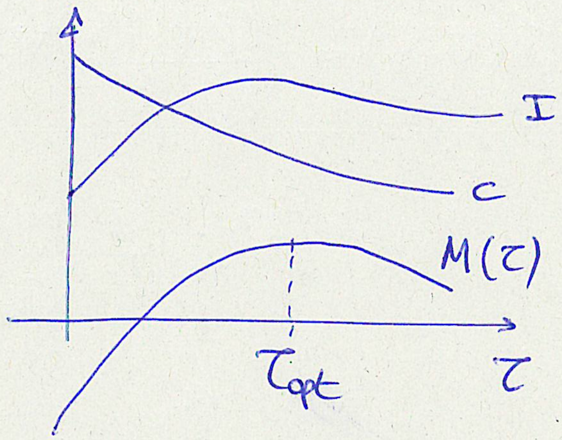
$$\frac{dM}{d\tau_{opt}} = 0 \qquad 0 = \frac{\left(\beta k_1 \exp(-k_1 \tau_{opt}) - 24 C_2\right)(\tau_{opt}+\tau_D) - \beta\left(1-\exp(-k_1 \tau_{opt})\right) +}{(\tau_D+\tau_{opt})^2}$$

$$\frac{-24\left(C_1 \tau_D + C_2 \tau_{opt} + C_3\right)}{(\tau_D + \tau_{opt})^2}$$

$\rightarrow \left(\beta k_1 \exp(-k_1 \tau_{opt}) - 24 C_2\right)(\tau_{opt}+\tau_D) - \beta\left(1-\exp(-k_1 \tau_{opt})\right) - 24\left(C_1 \tau_D + C_2 \tau_{opt} + C_3\right) = 0$

analytical solution is not available!
must be solved numerically

Alternatively, the M, C and I functions can be plotted and the maximum of M can be evaluated graphically



EXERCISE 3: parallel reactions in a CSTR

$$\begin{cases} A \xrightarrow{k_1} B \\ A \xrightarrow{k_2} C \end{cases}$$

B is the desired product

$k_1 = 0.5$ 1/min

$k_2 = 0.1$ 1/min

$Q = 4$ l/min

$C_A^{in} = 2$ mol/l

Selectivity $\sigma_B = \dfrac{C_B}{C_A^{in} - C_A}$ Yield $Y_B = C_B / C_B^{in}$

governing equations

$$\begin{cases} F_A^{in} - F_A + R_A V = 0 \\ F_B^{in} - F_B + R_B V = 0 \\ F_C^{in} - F_C + R_C V = 0 \end{cases}$$

$\rho =$ const

$$\begin{cases} C_A^{in} - C_A + R_A \tau = 0 \\ C_B^{in} - C_B + R_B \tau = 0 \\ C_C^{in} - C_C + R_C \tau = 0 \end{cases}$$

$$\begin{cases} C_A^{in} - C_A - K_{tot} C_A \tau = 0 \\ C_B^{in} - C_B + K_1 C_A \tau = 0 \\ C_C^{in} - C_C + K_2 C_A \tau = 0 \end{cases}$$

analytical solution

$$C_A^{in} - C_A - K_{tot} C_A \tau = 0$$

$$C_A (1 + K_{tot} \tau) = C_A^{in}$$

$$C_A = \frac{C_A^{in}}{1 + K_{tot} \tau}$$

$$C_B = C_B^{in} + K_1 C_A \tau \stackrel{!}{=} \frac{K_1 \tau C_A^{in}}{1 + K_{tot} \tau}$$

$$C_B = C_C^{in} + K_2 C_A \tau \stackrel{!}{=} \frac{K_2 \tau C_A^{in}}{1 + K_{tot} \tau}$$

$$\rightarrow \begin{cases} C_A = \dfrac{C_A^{in}}{1 + K_{tot} \tau} \\ C_B = \dfrac{K_1 \tau C_A^{in}}{1 + K_{tot} \tau} \\ C_C = \dfrac{K_2 \tau C_A^{in}}{1 + K_{tot} \tau} \end{cases}$$

selectivities

$$\begin{cases} \sigma_B = \dfrac{C_B}{C_A^{in} - C_A} = \dots = \dfrac{K_1}{K_{tot}} \\ \sigma_C = \qquad \dots \qquad = \dfrac{K_2}{K_{tot}} \end{cases}$$

yields

$$\begin{cases} Y_B = \dfrac{C_B}{C_B^{in}} = \dfrac{K_1 \tau}{1 + K_{tot} \tau} \\ Y_C = \dfrac{C_C}{C_C^{in}} = \dfrac{K_2 \tau}{1 + K_{tot} \tau} \end{cases}$$

maximization of yield of B

$$Y_B = \frac{k_1 \tau}{1 + k_{tot}\tau}$$

$$\frac{dY_B}{d\tau} = 0 \rightarrow \frac{dY_B}{d\tau} = \frac{k_1(1+k_{tot}\tau) - k_1 \tau k_{tot}}{(1+k_{tot}\tau)^2}$$

$$k_1(1+k_{tot}\tau) - k_1\tau k_{tot} = 0$$

$$k_1 + \cancel{k_1 k_{tot}\tau} - \cancel{k_1 \tau k_{tot}} = 0 \rightarrow \text{no max!}$$

EXERCISE 4: optimization of batch operations

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$T = 500\,K$

$V = 0.50\,m^3$

$N_A^\circ = 20\,kmol$

$\tau_D = 1\,h$

$$C_A^\circ = \frac{N_A^\circ}{V} = 40\,\frac{kmol}{m^3}$$

$k_1 = 1.75\ 1/h$

$k_2 = 0.0297\ 1/h$

governing equations

$$\begin{cases} \dfrac{dC_A}{dt} = -k_1 C_A \\ \dfrac{dC_B}{dt} = k_1 C_A - k_2 C_B \\ \dfrac{dC_C}{dt} = k_2 C_B \end{cases}$$

same solution of exercise 1

$$\begin{cases} C_A(t) = C_A^\circ \exp(-k_1 t) \\ C_B(t) = \dfrac{k_1 C_A^\circ}{k_2 - k_1}\left(\exp(-k_1 t) - \exp(-k_2 t)\right) \\ C_C(t) = C_A^\circ - C_B - C_A \end{cases}$$

Yield of B $\quad Y_B = \frac{C_B}{C_A^0} = \frac{k_1}{k_2-k_1}\left(\exp(-k_1 t) - \exp(-k_2 t)\right)$

$$\frac{dY_B}{dt} = 0 \quad \frac{k_1}{k_2-k_1}\frac{d}{dt}\left(\exp(-k_1 t) - \exp(-k_2 t)\right) = 0$$

$$\Downarrow \; \ldots$$

$$(k_2-k_1)\,t = \ln\frac{k_2}{k_1}$$

$$\Downarrow$$

$$t_{max}^B = \frac{\ln k_2/k_1}{k_2-k_1} \qquad t_{max}^B = \ldots = 2.37\,h$$

b) Optimal operation = max production of B

$$P_B \stackrel{def}{=} N_B(\tau_r)\cdot n_{cyc/day} = C_B(\tau)\cdot V \cdot \frac{24h}{\tau+\tau_D}$$

$$P_B(\tau) = \frac{24\cdot k_1 C_A^0 V}{k_2-k_1}\left[\exp(-k_1\tau) - \exp(-k_2\tau)\right] \Big/ (\tau+\tau_D)$$

$$\underline{|}\;\alpha\cdot\frac{\exp(-k_1\tau) - \exp(-k_2\tau)}{\tau+\tau_D}$$

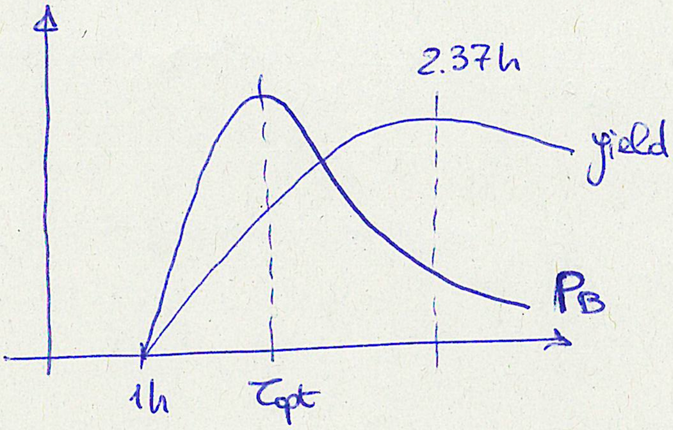
maximum production of B $\quad \frac{dP_B}{d\tau} = 0$

$$\frac{dP_B}{d\tau} = \alpha\,\frac{\left(-k_1\exp(-k_1\tau) + k_2\exp(-k_2\tau)\right)(\tau+\tau_D) - \left(\exp(-k_1\tau) - \exp(-k_2\tau)\right)}{(\tau+\tau_D)^2}$$

$$\left(-k_1\exp(-k_1\tau) + k_2\exp(-k_2\tau)\right)(\tau+\tau_D) = \exp(-k_1\tau) - \exp(-k_2\tau)$$

non linear algebraic equation
to be solved numerically in τ
to get τ_{opt}

graphical solution



$\tau_{opt} \simeq 0.79h$

EXERCISE 5: QSSA Hypothesis

Same exercise 1, only different numbers

iii) quasi-steady-state approximation for species B

if we look at the kinetic constants, we see that the second reaction is more than 1000 times FASTER than the first one

$K_1 = 0.57\ s^{-1}$

$K_2 = 1114\ s^{-1}$

$\frac{K_2}{K_1} \gg 1$ this means that B disappears as soon as it is produced

↓

we can assume B in QSS

$$\frac{K_2}{K_1} \gg 1 \rightarrow \frac{dC_B}{dt} \simeq 0 \rightarrow K_1 C_A \cong K_2 C_B$$

↓

$$C_B(\tau) = \frac{K_1}{K_2} C_A^0 \exp(-K_1 \tau)$$

Thus we have an explicit expression for C_B, instead of a differential equation.
This means that in principle the problem is described only by 2 differential equations, for A and C only

$$\begin{cases} \dfrac{dC_A}{dt} = -k_1 C_A \\ \dfrac{dC_C}{dt} = k_2 C_B = \dfrac{k_2 k_1}{k_2} C_A^0 \exp(-k_1 t) \end{cases}$$

$$\Downarrow$$

$$\begin{cases} \dfrac{dC_A}{dt} = -k_1 C_A \\ \dfrac{dC_C}{dt} = k_1 C_A^0 \exp(-k_1 t) \end{cases}$$

It is interesting to observe that k_2 does not appear in this set of equations!

Indeed, if $k_2 \gg k_1$, the RDS (RATE DETERMINING STEP) is the first reaction

$$\Downarrow$$

$$\begin{cases} C_A(t) = C_A^0 \exp(-k_1 t) \\ C_B(t) = C_A^0 \dfrac{k_1}{k_2} \exp(-k_1 t) \\ C_C(t) = C_A^0 (1 - \exp(-k_1 t)) \end{cases}$$

since $k_2/k_1 \gg 1$, C_B is expected to be always very small