

Chemical Reaction Engineering

Practical Session 1

15 November 2018

Multiple reactions

1. Parallel reactions in a CSTR

The species B is produced through an irreversible, first-order reaction $A \rightarrow B$ in liquid phase in a CSTR reactor. At the same time, a second unwanted reaction of degradation of A giving C occurs: $A \rightarrow C$. Determine the required volume to obtain 95% of A conversion, and the corresponding concentrations of B and C (volumetric inlet flow $Q = 4 \text{ l/min}$). Considering that the inlet flow contains 2 mol/l of A, evaluate yield and selectivity of B in such conditions. What is the required time to maximize the yield of B? And the selectivity?

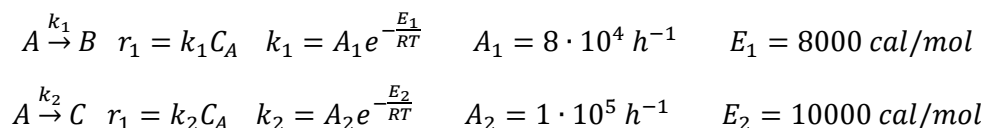
$$\begin{cases} r_1 = k_1 C_A \\ r_2 = k_2 C_A \end{cases} \quad \begin{cases} k_1 = 0.5 \text{ min}^{-1} \\ k_2 = 0.1 \text{ min}^{-1} \end{cases}$$

The yield and selectivity of B with respect to A are defined respectively as:

$$Y_B = \frac{C_B}{C_A^0} \quad \sigma_B = \frac{C_B}{C_A^0 - C_A}$$

2. Parallel reactions in a Batch reactor

The species B is produced from species A ($MW = 35 \text{ kg/kmol}$), according to the following kinetic mechanism, through which a secondary product C is formed, too:



The reaction is carried in liquid phase ($\rho = 800 \frac{\text{kg}}{\text{m}^3}$) at a temperature of 100°C .

Considering a conversion of A equal to 98%, evaluate the daily productivity of B, knowing that the reactor volume is $V = 1 \text{ m}^3$ and the overall downtime for reactor loading, unloading and cleaning is $t_D = 1 \text{ h}$.

Knowing that the operating costs C_F for single cycle vary according the cost function reported below (as function of downtime and residence time), evaluate the optimal conversion of A, and the corresponding daily productivity of B. The revenue obtained from product selling are equal to $15 \text{ \$/kg}$.

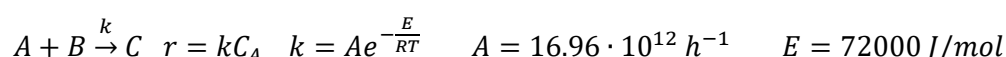
$$C_F(\tau) = C_1 t_D + C_2 \tau + C_3 \quad \begin{cases} C_1 = 100 \text{ \$/h} \\ C_2 = 25 \text{ \$/h} \\ C_3 = 8000 \text{ \$} \end{cases}$$

Non isothermal reactors

3. Production of propylene glycol

Propylene glycol (C) is produced from the hydrolysis of propylene oxide (A) in a steady, **perfectly stirred reactor**. To this purpose, a reactor with a volume of 1135 l is used. The reactants are fed to the reactor through two streams: the first is made up of propylene oxide (A) and methanol (M), in equivolometric quantities, each of 1320 l/h. The second is made up of water (B) and is equal to 6600 l/h. The corresponding molar flows of propylene oxide, methanol and water are equal to 19.50 kmol/h, 32.6 kmol/h and 364 kmol/h. The temperature of the two streams is 14°C, but after their mixing (before entering the reactor) and increment of 10 °C is observed.

The reaction can be considered as irreversible and first-order with respect to propylene oxide (A), and of order zero with respect to water (B):



The reactor must operate at a temperature not higher than 53 °C, in order to be sufficiently far away from the boiling point of propylene oxide.

Is then possible using the reactor with this constraint on temperature? Which would be the corresponding propylene oxide conversion?

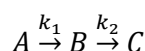
Constant-pressure specific heats are indicated in the table below, as well as the enthalpy of formation of the different compounds. The variation of density of the liquid (which is experimentally known as ~3%) can be ignored.

Specific heat in J/mol/K	
Cp_A	146
Cp_B	75
Cp_C	192
Cp_M	82

Formation enthalpy in J/mol	
$H_A(20^\circ\text{C})$	-148918
$H_B(20^\circ\text{C})$	-275000
$H_C(20^\circ\text{C})$	-505360

Numerical model of an isothermal plug flow reactor

4. Build up the numerical model of a plug flow reactor, with an internal diameter of 8 cm and a length of 100 m. The following reactions occur within the PFR:



The reactor works at a temperature of 750 °C, a pressure of 3 bar and is fed by a molar flow of A ($MW = 25 \text{ kg/kmol}$) equal to 20 kmol/h.

Considering both the reactions as first-order:

$$\begin{cases} r_1 = k_1 C_A \\ r_2 = k_2 C_B \end{cases} \quad \begin{cases} k_1 = A_1 e^{-\frac{E_1}{RT}} & A_1 = 1.2 \cdot 10^8 \text{ s}^{-1} & E_1 = 37000 \text{ cal/mol} \\ k_2 = A_2 e^{-\frac{E_2}{RT}} & A_2 = 4 \cdot 10^8 \text{ s}^{-1} & E_2 = 39000 \text{ cal/mol} \end{cases}$$

evaluate the concentration profiles of the different compounds throughout the reactor. Do this in two ways:

- i. Analytical resolution of the differential system.
- ii. Numerical resolution of the differential system through one of the ODE solvers available in MATLAB®.

Compare the obtained yield in C in both the approaches.

Suggested exercises

Numerical model of an isothermal plug flow reactor

5. Repeat the previous exercise (#4) considering the new set of kinetic parameters:

$$\begin{cases} r_1 = k_1 C_A \\ r_2 = k_2 C_B \end{cases} \quad \begin{cases} k_1 = A_1 e^{-\frac{E_1}{RT}} & A_1 = 2 \cdot 10^8 \text{ s}^{-1} & E_1 = 40000 \text{ cal/mol} \\ k_2 = A_2 e^{-\frac{E_2}{RT}} & A_2 = 4 \cdot 10^8 \text{ s}^{-1} & E_2 = 26000 \text{ cal/mol} \end{cases}$$

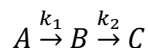
In particular, evaluate the species concentration profiles in three ways:

- i. Analytical solution of the differential system.
- ii. Numerical resolution of the differential system through one of the ODE solvers available in MATLAB®.
- iii. Numerical resolution of the differential system through the hypothesis of pseudo steady-state of B.

Compare the yield of C obtained with the three methods, and evaluate the distance between the analytical and the numerical resolution in terms of maximum error on C_B .

Design/Simulation of a batch reactor

6. Starting from species A, the species B must be produced in an isothermal batch reactor:



The kinetic constants k_1 and k_2 are respectively:

$$\begin{cases} k_1 = A_1 e^{-\frac{E_1}{RT}} & A_1 = 1.5 \cdot 10^4 \text{ h}^{-1} & E_1 = 9000 \text{ cal/mol} \\ k_2 = A_2 e^{-\frac{E_2}{RT}} & A_2 = 6 \cdot 10^6 \text{ h}^{-1} & E_2 = 19000 \text{ cal/mol} \end{cases}$$

The reactor works at a temperature of 500 K with a liquid mixture. Its volume is 0.5 m³, and at the beginning of each cycle 20 kmol of A are introduced.

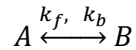
Knowing that the total time required for reactor loading, unloading, and cleaning is 1 h:

- i. Evaluate the reaction time to maximize the yield of B.
- ii. Define the optimal conditions to maximize the daily production of B. In detail, evaluate:
 - cycle length (sum of reaction and downtimes)
 - conversion of A per cycle
 - number of cycles per day

– daily production of B

Design of flow reactors for isomerization

7. Species A is to be isomerized to species B in a plug-flow reactor, according to the following elementary reversible reaction:



where k_f and k_b are the kinetic constants of forward and backward constants, respectively. The forward kinetic constant is equal to 31.1 h^{-1} at 360 K , and its activation energy is 65700 J/mol . The equilibrium constant K_{eq} is equal to 3.03 at 60°C .

The inlet mixture is fed at 330 K , with a volumetric flow rate of 163 kmol/h . Its molar composition is equal to 90% of species A and 10% of inert species (I). The inlet concentration of A is 9.30 kmol/m^3 .

The reaction heat, measured at the reference temperature of 300 K , is $-6900 \frac{\text{J}}{\text{mol}}$. The constant-pressure specific heats of species are independent of temperature: $C_p^A = 131, C_p^B = 171, C_p^I = 161 \frac{\text{J}}{\text{mol K}}$.

Calculate the PFR volume necessary to convert 60% of species A and compare it to the volume of a CSTR working in the same conditions.