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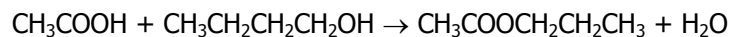
Exercises of "*Fundamentals of Chemical Processes*"

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EXERCISE 11

Reactor for the esterification of butanol

The following data were obtained in a homogenous batch reactor for the esterification of butanol (B) with acetic acid (A):



The experiments were carried out at a 100°C, starting from the following initial conditions:

$$A^0 = 0.2332 \text{ mol} \quad B^0 = 1.1600 \text{ mol}$$

The data collected during the experiments are reported in the table below. The batch volume is equal to 120 cm³. Determine the parameters of the power law type kinetic equation that describes the experimental results. Furthermore, assume that the reaction is also carried out in a flow-type reactor. Specifically, compare the results obtained in the case of a CSTR reactor and a PFR reactor. At the inlet of the reactor, the flow rate of acetic acid is 1 mol/h (MM = 60 g/mol, density = 1050 kg/m³) and that of butanol is 5 mol/h (MM = 74 g/mol, density = 810 kg/m³). Assuming that the mixture is ideal and that the total volumetric flow rate (acetic acid and butanol) maintains constant, estimate the volume required by each reactor in case the target conversion of acetic acid is 32%.

Data

t [h]	Converted moles of A
0	0
1	0.01636
2	0.02732
3	0.03662
4	0.04525
5	0.05405
6	0.06086
7	0.06833
8	0.07398

Solution

The reaction rate (r) is expressed by a power law type expression:

$$r = k \cdot C_A^\alpha \cdot C_B^\beta$$

Given that the consumption stoichiometry is equimolar, at the end of the reaction 0.07398 mol of butanol are converted. Therefore, the amount of butanol maintains almost constant, passing from 1.16 mol at the beginning, to 1.086 mol at the end of the reaction. The concentration of butanol C_B can be assumed as constant during the experiment. Based on the data, it is not possible to determine the value of the exponent of C_B . It is then possible to include C_B in the reaction constant.

$$r = k^* \cdot C_A^\alpha$$

The material balance on the batch reactor is written as:

$$\frac{dn_A}{dt} = -r \cdot V = -k^* \cdot C_A^\alpha \cdot V = -k^* \cdot \frac{n_A^\alpha}{V^\alpha} \cdot V = -k^* \cdot n_A^\alpha \cdot V^{1-\alpha} = -K \cdot n_A^\alpha$$

$$K = k \cdot C_B^\beta \cdot V^{1-\alpha}$$

The data at disposal are expressed as moles of acetic acid, not in terms of concentration. Despite the volume of the batch reactor is known, it is convenient to rearrange the material balance in order to include the reactor volume in the K constant. Also, the data are in integral form, whereas the material balance is in differential form. It is then possible to:

- 1) turn the data into a differential form, by application of the finite difference approach; in this way, the uncertainty due to the finite difference approximation is introduced in the estimates;
- 2) turn the material balance equation into an integral form (and, if possible, into an analytic form); this approach however increases the complexity of the parameter estimation, via non-linear regression.

In the following, the parameters are determined via the rearrangement of the integral data into differential data, followed by a linear regression on the expression of the material balance into a logarithmic form:

$$\ln\left(-\frac{dn_A}{dt}\right) = \ln(K) + \alpha \cdot \ln(n_A)$$

The rate of consumption of the acetic acid dn_A/dt is determined as follows:

$$y_+ = \frac{y(x + \Delta x) - y(x)}{\Delta x}$$

$$y_- = \frac{y(x) - y(x - \Delta x)}{\Delta x}$$

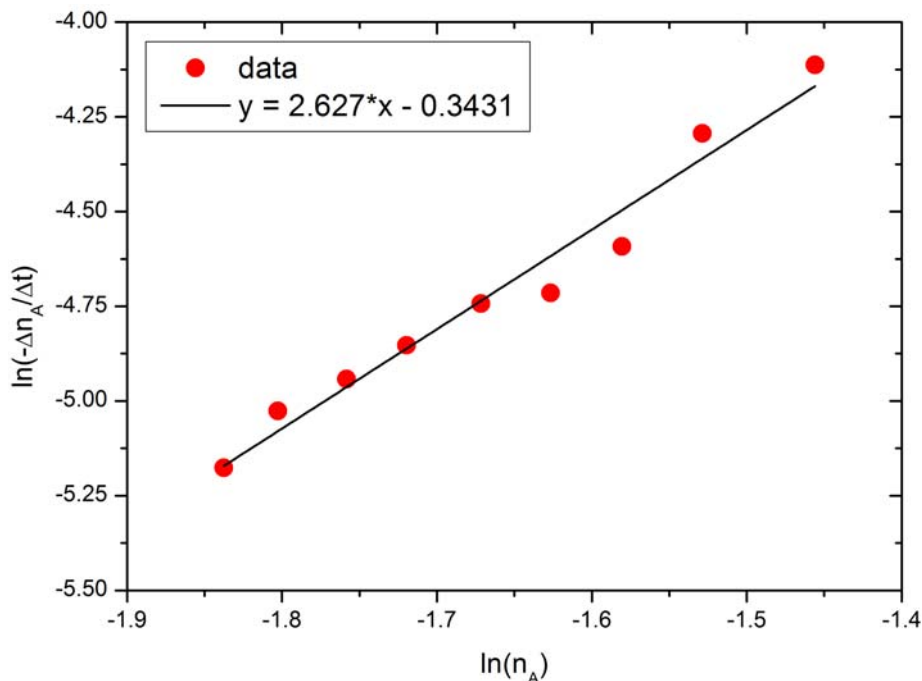
$$y_\pm = \frac{y(x + \Delta x) - y(x - \Delta x)}{2 \cdot \Delta x}$$

In the initial instant of the reaction ($t = 0$), the y_+ expression must be used. In the final instant ($t = 8h$), the expression y_- must be used. It is important to note also that the data are expressed in term of moles of converted acetic acid. At every instant t of the reaction, the moles of acetic acid present in the system are calculated as follows:

$$mol_A = mol_A^0 - mol_A^{conv}$$

The results are reported in the table and in the plot below.

t [h]	moles of A converted	moles of A	r _A [mol/h]	ln(-r _A)	ln(n _A)	K verify
0	0	0.23320	-0.01636	-4.11292	-1.45586	0
1	0.01636	0.21684	-0.01366	-4.29328	-1.52860	0.82578
2	0.02732	0.20588	-0.01013	-4.59225	-1.58046	0.73864
3	0.03662	0.19658	-0.00896	-4.71443	-1.62669	0.70204
4	0.04525	0.18795	-0.00872	-4.74271	-1.67158	0.69096
5	0.05405	0.17915	-0.00781	-4.85299	-1.71953	0.70432
6	0.06086	0.17234	-0.00714	-4.94204	-1.75829	0.69645
7	0.06833	0.16487	-0.00656	-5.02676	-1.80260	0.71180
8	0.07398	0.15922	-0.00565	-5.17610	-1.83747	0.70716



The linear interpolation gives the following kinetic parameters:

$$\alpha = 2.627$$

$$K = \exp(-0.3431) = 0.709 \frac{1}{mol^{1.627} \cdot m^3 \cdot h}$$

The K constant includes also the volume of the reactor (expressed in m³). The constant k* is then determined: it includes the reaction constant and the term C_B raised to the reaction order β.

$$K = k \cdot C_B^\beta \cdot V^{1-\alpha}$$

$$k^* = k \cdot C_B^\beta = \frac{K}{V^{1-\alpha}} = 2.961 \cdot 10^{-7} \frac{m^{4.881}}{mol^{1.627} \cdot h}$$

It is worthy to note that the units of the k* constant do not express a physically sound relation, but are a consequence of the fact that the global rate has the units of mol/m³/h. It is finally possible to verify whether or not the estimates of the kinetic parameters are correct, by transforming the material balance equation

into an integral form. Given the value of the reaction order α , it is possible to integrate the material balance equation:

$$\frac{dn_A}{n_A^\alpha} = -K \cdot dt$$

$$\int_{n_A^0}^{n_A} \frac{dn_A}{n_A^\alpha} = -K \cdot t \quad t_0 = 0$$

$$\frac{1}{1-\alpha} \cdot n_A^{1-\alpha} \Big|_{n_A^0}^{n_A} = -K \cdot t$$

$$K = \frac{n_A^{1-\alpha} - n_{A,0}^{1-\alpha}}{(\alpha-1) \cdot t} = \frac{n_A^{-1.627} - n_{A,0}^{-1.627}}{1.627 \cdot t}$$

In the last column of the table, the values of the K constant estimated via the integral form are reported. The arithmetic average of the K values (excluding the initial null value) leads to an estimate equal to 0.722, which verifies the hypotheses of the linear equation.

In the second part of the problem, the same reaction is assumed to be performed in a CSTR and in a PFR. The problem asks for the estimation of the volume of each reactor. The kinetic equation is kept unaltered with respect to the batch problem. Before writing the material balance for each reactor, it is convenient to evaluate the volumetric feed flow rate Q^0 . Given that the liquid mixture is ideal (that is, there are no variations of the volume as a consequence of the mixing of the two currents), the volumetric flow rate is obtained from the molar masses and the densities of the species:

$$Q = \frac{F_A^0 \cdot PM_A}{\rho_A} + \frac{F_B^0 \cdot PM_B}{\rho_B} = 5.139 \cdot 10^{-4} \text{ m}^3/\text{h}$$

In the case of the CSTR, the material balance is:

$$F_A - F_A^0 = \nu_A \cdot R \cdot V_{CSTR} = -k^* \cdot (C_A)^\alpha \cdot V_{CSTR}$$

It is important to note that the reaction rate in the CSTR balance is a function of the outlet concentration C_A of the stream F_A at that exits the reactor. It is also possible to express the physical quantities present in the balance as a function of the conversion of the acetic acid and of the volumetric flow rate of the intel feed Q :

$$\chi_A = \frac{F_A^0 - F_A}{F_A^0}$$

From which one obtains:

$$F_A - F_A^0 = -\chi_A \cdot F_A^0$$

The estimation of the concentration leads to:

$$C_A = \frac{F_A}{Q}$$

$$C_A^0 = \frac{F_A^0}{Q^0} = 1945.78 \text{ mol/m}^3$$

Only in case the total volumetric flow rate Q is constant (i.e. $Q^0 = Q$), it is possible to estimate C_A based on the conversion as a function of the concentration, as follows:

$$C_A = C_A^0 \cdot (1 - \chi_A)$$

By substitution of the latter relation in the balance equation, it results:

$$\chi_A \cdot F_A^0 = -K \cdot (C_A^0)^\alpha \cdot (1 - \chi_A)^\alpha \cdot V_{CSTR}$$

From which, it is obtained:

$$V_{CSTR} = \frac{\chi_A \cdot F_A^0}{K \cdot (C_A^0)^\alpha \cdot (1 - \chi_A)^\alpha}$$

In the problem, the volume of the CSTR results equal to 6.81 liters. Additionally, it is possible to estimate the residence time inside the reactor:

$$\tau = \frac{V_{CSTR}}{Q} = 13.25 \text{ h}$$

In the case of the PFR reactor, the balance equation is:

$$\frac{dF_A}{dV_{PFR}} = v_A \cdot R = -k^* \cdot (C_A)^\alpha$$

In the equation, the reaction rate is a function of the concentration C_A of the stream F_A , which is varying along the reactor volume, starting from the feed section up to the outlet section. By assuming that the total volumetric flow rate is constant, and by substituting the concentration as a function of the conversion, it results:

$$dF_A = -F_A^0 \cdot d\chi_A$$

$$-\frac{F_A^0 \cdot d\chi_A}{dV_{PFR}} = -K \cdot (C_A^0)^\alpha \cdot (1 - \chi_A)^\alpha$$

The equation has to be integrated between 0 and the final conversion $\chi_{A,f}$ (equal to 90%), obtaining:

$$\frac{d\chi_A}{(1-\chi_A)^\alpha} = \frac{K \cdot (C_A^0)^\alpha}{F_A^0} \cdot dV_{PFR}$$

$$\int_0^{\chi_{A,f}} \frac{d\chi_A}{(1-\chi_A)^\alpha} = \frac{K \cdot (C_A^0)^\alpha}{F_A^0} \cdot V_{PFR}$$

$$V_{PFR} = -\frac{F_A^0}{K \cdot (C_A^0)^\alpha} \cdot \frac{1}{1-\alpha} \cdot [(1-\chi_{A,f})^{1-\alpha} - 1]$$

The volume of the PFR is equal to 4.36 liters. As in the previous case, the residence time is estimated as:

$$\tau = \frac{V_{PFR}}{Q} = 8.07h$$

It is important to note that the residence time in the PFR is lower than that obtained in the CSTR, at equal outlet conversion of the acetic acid. This result is coherent with the fact that, in the case of the CSTR, the reaction rate is evaluated at the outlet conditions in the whole volume of the reactor (specifically, C_A is the relevant quantity) and therefore the reaction rate value is always lower than that obtained in the PFR balance, which varies from the highest value at the inlet concentration (C_A^0) to the lowest value at the outlet concentration (C_A).