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Investigation of chemical reactors

INTRODUCTION

For the design, scale-up, optimal operation of chemical reactors, the knowledge of the effect of reactor volume, temperature, reaction rate, feed rate on the conversion is of fundamental importance. The conversion can be calculated easily when simplified models are used to describe flow patterns and mixing caracteristics in the reactors. Further on the stirred tank reactor, both batch and continuous, and the plug flow tubular reactor will be investigated. Only homogenouos systems and single reactions are considered.

THERORY

Ideally stirred batch reactor

The reactants are fed into the reactor, then the reactor operates during a period of time what is needed for the desired conversion. After the process the reactant mixture is removed from. In ideal case stirring is so efficient, that concentration, temperature and all the other physico-chemical parameters have the same value at any point in the reactor. Because of this uniformity of concentration and temperature, the material and heat balances may be written over the entire reactor volume:

$$\nu_i r V = \frac{dn_i}{dt} \qquad (1)$$

$$rV(-\Delta H_r)-hF(T-\bar{T}_h)=V\rho c_p\frac{dT}{dt} \qquad (2)$$

where

ν_i	stoichiometric coefficient,
r	reaction rate ($mol/m^3/s$),
V	volume of reacting mixture (m^3),

(In case of reaction in the liquid phase the volume of the reactor is always larger).

n_i	number of moles of component i (mol),
t	holding time (s),
$(-\Delta H_r)$	heat of reaction (J/mol),
h	heat transfer coefficient ($W/m^2/K$),
F	heat transfer area (m^2),
T	temperature of reacting mixture (K),
T_h	cooling/heating agent average temp. (K),
ρ	density (kg/m^3),
c_p	specific heat (J/kg/K)

The two balance equations can be solved simultaneously by computer, numerically. Computation is more simple in isotherm or adiabatic case. In isotherm operation the temperature is constant during the reaction time. It is not an easy task because the amount of heat to transfer is decreasing in time. Isotherm conditions can be reached without difficulties when reaction heat or reaction rate is small. For isothermal systems, temperature is being constant Eq. (1) can be integrated if the reaction rate is known.

$$t=\int_{n_{io}}^{n_i}\frac{dn_i}{\nu_i rV}=n_{io}\int_0^{X_i}\frac{dX_i}{|\nu_i| rV} \qquad (3)$$

where n_{io} is the initial quantity of component i (mol),

$X_i=\frac{n_{io}-n_i}{n_{io}}$ the fraction conversion for an initial component not in excess.

If the reacting volume is constant Eq. (3) can be read as

$$t = \int_{c_{io}}^{c_i} \frac{dc_i}{\nu_i r} = c_{io} \int_{0}^{X_i} \frac{dX_i}{|\nu_i| r} \qquad (4)$$

where c_i is the concentration of component i.
In case of simple rate equations integration of Eq. (4) can be made analytically as it is shown in Table 1.
Under adiabatic operation conditions there is no heat interaction between the reactor contents and their surroundings. In small-scale equipments because of the relatively large specific heat transfer area adiabatic operation can be carried out only by very careful isolation. There is no analytical solution (except for simple-order rate forms) when integrating Eq. (3) and (4) because in the rate equation due to the Arrhenius equation the rate coefficient is an exponential function of temperature.

$$k = Ae^{-\frac{E}{RT}} \qquad (5)$$

where A pre-exponential coefficient,
E activation engergy (J/mol),
R gas constant (8.314 J/mol/K).

Substituting the reaction rate from Eq. (1) to Eq. (2) the temperature change can be written as

$$T-T_0 = \frac{(-\Delta H_r)}{\nu_i \varrho c_p} \int_{c_{io}}^{c_i} dc_i = \frac{(-\Delta H_r) c_{io}}{|\nu_i| \varrho c_p} X_i \qquad (6)$$

Continuous stirred tank reactor (CSTR)

The in- and outflowing rate and so the reacting volume is constant in time. In case of ideal mixing the inflowing reactans are immediately (in a time interval that is very small compared to the mean residence time) mixed with the reacting mixture so that the system properties are uniform throughout the reactor. Due to the perfect mixing the effluent composition and

Design equations for isothermal batch and plug flow tubular reactors

Table 1.

Reaction	Order	X (conversion)	$\bar{t}$ (Time)
$A \rightarrow P$ (products)	0	$\frac{k\bar{t}}{c_{Ao}}$	$\frac{c_{Ao}X}{k}$
	1	$1-e^{-k\bar{t}}$	$-\frac{1}{k}\ln(1-X)$
	μ	$1-\left[1+(\mu-1)k\bar{t}c_{Ao}^{\mu-1}\right]^{\frac{1}{1-\mu}}$	$\frac{(1-X)^{1-\mu}-1}{k\,c_{Ao}^{(\mu-1)}\cdot(\mu-1)}$
$2A \rightarrow P$ $A+B \rightarrow P\ (c_{Ao}=c_{Bo})$	2	$\frac{k\bar{t}\,c_{Ao}}{1+k\bar{t}c_{Ao}}$	$\frac{1}{k\,c_{Ao}}\quad\frac{X}{1-X}$
$A+B \rightarrow P(c_{Ao}<c_{Bo})$	2	$\frac{c_{Bo}\left(e^{k\bar{t}(c_{Ao}-c_{Bo})}-1\right)}{c_{Ao}e^{k\bar{t}(c_{Ao}-c_{Bo})}-c_{Bo}}$	$\frac{1}{k(c_{Ao}-c_{Bo})}\cdot\ln\frac{c_{Bo}(1-X)}{c_{Bo}-c_{Ao}X}$
$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B\ (c_{Bo}=0)$	1	$\frac{k_1}{k_1+k_2}\left(1-e^{-(k_1+k_2)\bar{t}}\right)$	$-\frac{1}{k_1+k_2}\ln\left(1-X-\frac{k_2}{k_1}X\right)$

temperature are thus identical with those of the reactor contents. The steady-state component and heat balance:

$$\dot{n}_{io}-\dot{n}_i+\nu_i rV = 0 \tag{7}$$

$$W\rho c_p(T_o-T)-hF(T-\bar{T}_h)+rV(-\Delta H_r)=0 \tag{8}$$

where $\dot{n}_i$ molar flowrate of component i (mol/s),
W feed rate (m^3/s),
o subscript referring to initial conditions.

Under isotherm operation Eq. (7) component balance is to be solved. Supposing that the reacting volume is constant

$$Wc_{io}-Wc_i+\nu_i rV = 0 \tag{9}$$

For some simple rate equations expressions for the mean residence times ($\bar{t}$) required to achive a given conversion are summarised in Table 2.
Under adiabatic operating conditions the heat balance reads as

$$W\rho c_p(T-T_o)=rV(-\Delta H_r) \tag{10}$$

The nonlinear equation system (9) and (10) can be solved numericaly or graficaly. The heat generated by the reaction

$$q_r = rV(-\Delta H_r) \tag{11}$$

And the convective heat

$$q_o = W\rho c_p(T-T_o) \tag{12}$$

is plotted against temperature on Fig.1. The

Design equations for CSTR

Table 2.

Reactions	Order	$\frac{c_A}{c_{Ao}} = 1-X$	$\bar{t}$
$A \rightarrow P$ (products)	0	$1-\frac{k\bar{t}}{c_{Ao}}$	$\frac{c_{Ao}X}{k}$
	μ	$\frac{1}{1+kc_A^{\mu-1}\bar{t}}$	$\frac{1}{k\,c_{Ao}^{\mu-1}} \frac{X}{(1-X)^{\mu}}$
$2A \rightarrow P$ $A+B \rightarrow P(c_{Ao}=c_{Bo})$	2	$\frac{-1+\sqrt{1+4k\bar{t}c_{Ao}}}{2k\bar{t}c_{Ao}}$	$\frac{1}{kc_{Ao}} \cdot \frac{X}{(1-X)^2}$
$A+B \rightarrow P(c_{Ao}<c_{Bo})$	2	$\frac{-b+\sqrt{b^2+4k\bar{t}c_{Ao}}}{2k\bar{t}c_{Ao}}$ where $b=1+(c_{Bo}-c_{Ao})k\bar{t}$	$\frac{X}{k(1-X)(c_{Bo}-Xc_{Ao})}$
$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B(c_{Bo}=0)$	1	$\frac{1+(k_1+k_2)\bar{t}(1-X^*)}{1+(k_1+k_2)\bar{t}}$ where $X^* = \frac{c_{Ao}-c_{Ae}}{c_{Ao}}$ c_{Ae} equilibrium concentration	$\frac{X}{(k_1+k_2)(X^*-X)}$

intersection is the operating point of the reactor. Knowing the operating temperature the mean residence time (V/W) or the conversion can be calculated from Eq. (7) or (9). For a given conversion the temperature in the reactor can be derived by solving Eq. (9) and (10).

$$T-T_o = \frac{c_{io} (-\Delta H_r)}{\rho c_p |\nu_i|} X_i \qquad (13)$$

Under polytropic conditions (cooled or heated reactor) the operating point can be derived with the same procedure by solving Eq. (8) and (9). Taking into consideration that a part of the generated heat is removed through the wall Eq. (12) reads as

$$rV(-\Delta H_r)=W \rho c_p(T-T_o)+hF(T-\overline{T}_h) \qquad (14)$$

The right-hand side represents the net heat removed by both flow and external heat exchange. The solution to Eq. (14) can be obtained by plotting both sides against T and noting the intersection of the curves.

Plug flow tubular reactor (PFR)

The main assumption is that the flow is of plug flow or piston flow mechanism. At any point in a cross section of the reactor all the parameter values (temperature, concentration, pressure) are indentical. The residence time for all the fluid elements is the same, therefore so is the conversion in every fluid element. Since the fluid composition varies with longitudinal position we must write the balance equations for a section of length dl (Fig.2.)

$$-Wdc_i + \nu_i rdV=0 \qquad (15)$$

$$-W \rho c_p dT-h(T-\overline{T}_h dF+rdV(-\Delta H_r) = 0 \qquad (16)$$

where dV=Adl infinitesimal reactor volume (m^3),

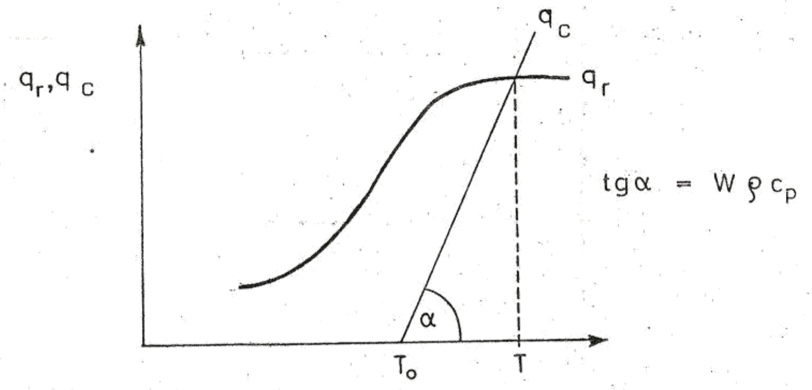


Figure 1.

Rate of heat generated or removed by chemical reactions under adiabatic operating conditions

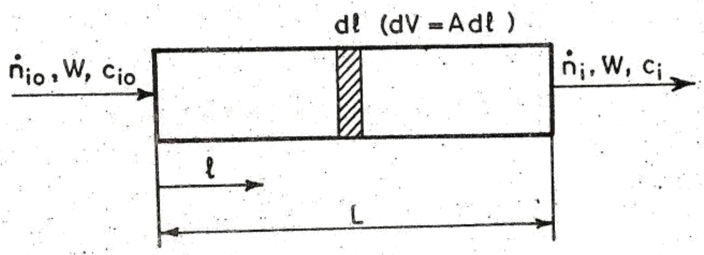


Figure 2.

Tubular reactor

A	cross section (m^2),
D	reactor diameter (m),
l	length coordinate (m),
dF	infinitesimal heat transfer area (m^2).

Generally Eq. (15) and (16) can only be solved numerically. Under isotherm operation from the component balance (Eq. (15)), the residence time is

$$\bar{t} = \frac{V}{W}\int_0^{c_i}\frac{dc_i}{\nu_i r} = c_{io}\int_0^{X_i}\frac{dX_i}{|\nu_i| r} \qquad (17)$$

The form of this equation is the same as Eq. (4) for the batch reactor, so the results summarised in Table 1. can be used. The only difference is that t means the residence time instead of the holding time.
In an adiabatic PFR the heat balance is

$$-W \rho c_p dT + r dV(-\Delta H_r) = 0 \qquad (18)$$

Substituting the reaction rate from Eq. (15) to Eq. (18) the same formula as Eq. (6) can be get, so the adiabatic PFR can be calculated as it was shown in the case of batch reactors.

THE REACTION INVESTIGATED

The reaction between sodium hydroxide (NaOH) and ethyl acetate in aqueous solution was chosen since the kinetics are well-known, the rate constants are well established and a simple analytical technique can be used. The saponification reaction has been shown to be bimolecular and second order. The reaction is

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

In the chosen concentration and temperature interval the reverse reaction is assumed to be negligible, so the rate is

$$r = kc_Ac_B \tag{19}$$

where c_A is the concentration of component A being not in excess (mol/m^3).
The temperature dependence of the rate coefficient is

$$\ln k = 20{,}8-5640/T \quad \text{and } k \left(\frac{dm^3}{mol.min}\right) \tag{20}$$

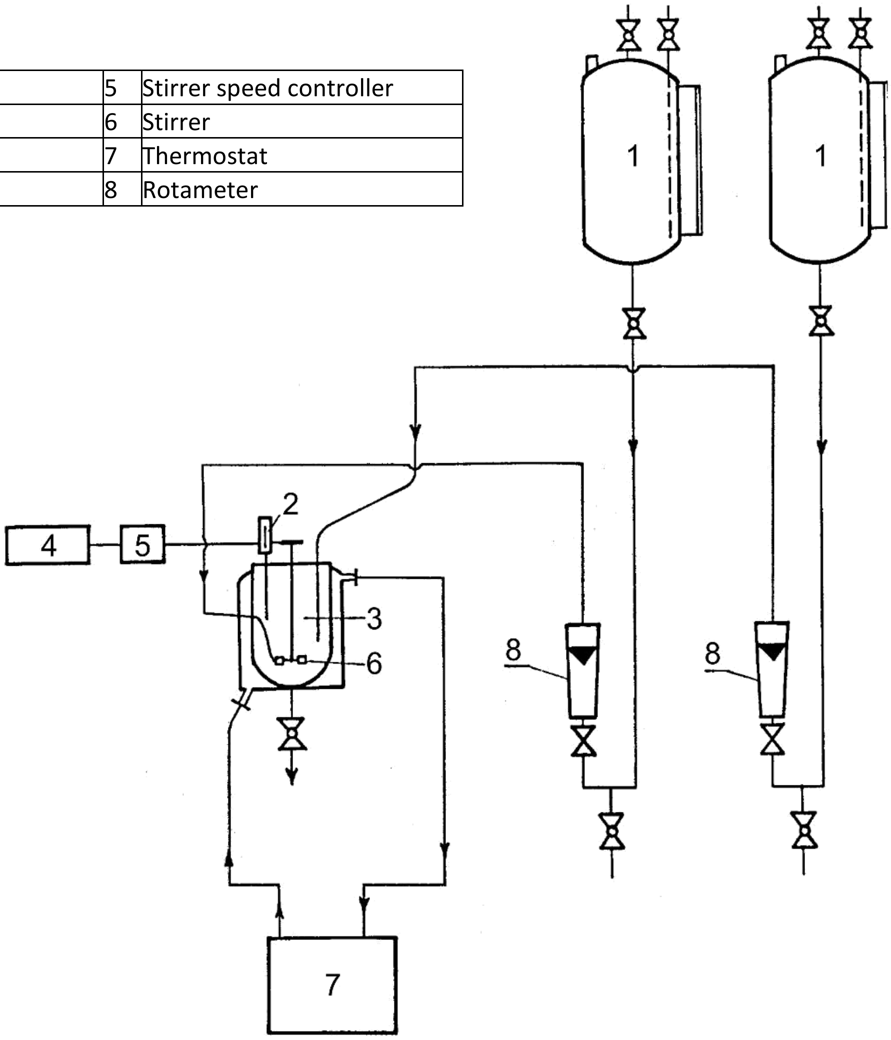
EQUIPMENT

The experimental set-up is shown on Fig.3. The reactants can be introduced through rotameters from two storage tanks (30 L each, made of acidproof steel). With three-way cocks both the tank or the tube reactor can be operated.

<u>The tank reactor:</u>

Reactor I.D. 148 mm,
Height of reacting mixture 180 mm,
Distance of stirrer from the bottom 63 mm,
Six flat-blade turbine diameter 49.6 mm,
Volume 3 dm^3.
The tank is made of KO 36 acidproof steel. The impeller speed is controlled using a DANFOSS VLT-1 speed governer.

1	Feed tank	5	Stirrer speed controller
2	Thermometer	6	Stirrer
3	Stirred tank reactor	7	Thermostat
4	motor / engine	8	Rotameter



PROCEDURE

The operational procedure for the flow reactors is in brief as follows:

- Adjustment of reactant flow rates using rotameter calibration charts. Flow rates are controlled manually through the course of the runs.
- Heating reactants to the desired reaction temperature (25-35 ^{0}C). For this purpose thermostats are used.
- Obtaining reaction samples. Once the reactants flow rates and temperatures have been established at the desired level operation is continued to obtain steady state conditions. Samples are then taken at 5 minute intervals from the reactor effluent. Sample is collected in a weighed flask containing a known amount of 0.1 mol/l HCl solution. The reaction sample is always kept small enough so that the HCl will be in excess. The flask is weighed again to determine the amount of the sample.
- Analysis of reaction mixture. The extent of reaction between the NaOH and ethyl acetate is determined by titrating the excess HCl, used to quench the mixture, with standardized NaOH. By knowing the amount of NaOH originally present in the feed and the amount present in the effluent, the degree of reactant conversion is determined.
- Obtaining inlet composition. Samples are taken from the reactant flows. The exact composition of the NaOH solution is determined by titrating with 0,1 mol/l HCl. The composition of the ethyl acetate solution is determined by reacting it with an excess of NaOH and titrating the unreacted NaOH with standard HCl solution. This is done by mixing 20 ml of ethyl acetate

solution with 30 ml of standard NaOH solution and allowing the mixture to react for about 1/2 hour on a water bath. At the end of this time, when the reaction is assumed to have gone to completion, standard HCl is used to measure the amount of unreacted NaOH. The remainder of the NaOH is assumed to have reacted with ethyl acetate, and thus, the ethyl acetate concentration can be determined.

TREATMENT OF DATA

1. Calculate fraction conversion (X) of the reactant being not in excess from the measured data

$$X = \frac{c_{Ao}-c_A}{c_{Ao}}$$