5.4
Tubular Reactor Examples

5.4.1
TUBE and TUBEDIM – Tubular Reactor Model for the Steady State

System

The tubular reactor, steady-state design equation is of interest here. The dimensional and dimensionless forms are compared for the case of an nth-order reaction.

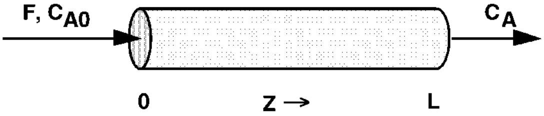

Fig. 1 Isothermal tubular reactor.

Model

The component mass balance at steady state is

$$\frac{dC_A}{dZ} = \frac{1}{v} r_A$$

where v is the linear flow velocity (= F/A).

The kinetics here are

$$r_A = -kC_A^n$$

Using the variables $\overline{C_A} = C_A/C_{A0}$ and $\overline{Z} = Z/L$, the dimensionless model is

$$\frac{d\overline{C_A}}{d\overline{Z}} = \left[\frac{kL}{v} C_{A0}^{n-1}\right] \overline{C_A^n} = [PAR]\overline{C_A^n}$$

Note that the dimensionless parameter PAR is the ratio of the residence time, L/v, and the reaction time for an nth-order reaction, $1/kC_{A0}^{n-1}$.

Program

The results for both the separate dimensional TUBE and dimensionless TUBEDIM cases should be the same if the reaction order n and PAR are the same.

Chemical Engineering Dynamics: An Introduction to Modelling and Computer Simulation, Third Edition
J. Ingham, I.J. Dunn, E. Heinzle, J.E. Prenosil, J.B. Snape
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Nomenclature

Symbols

A	Area of tube cross-section	m^2
C_A	Concentration	$kmol/m^3$
F	Flow rate	m^3/s
k	Rate constant	various
n	Reaction order	–
r_A	Reaction rate	$kmol/m^3\ s$
t	Time	s
v	Flow velocity	m/s
Z	Length	m

Exercises

1. Run TUBE for various k, v and C_{A0} and compare with corresponding runs from TUBEDIM.
2. Graph $\overline{C_A}$ versus $\overline{Z}$ n=1 for and various values of PAR.
3. Repeat Exercise 2 for n=2.

Results

Using the same set of parameters, the results from both programs will be the same.

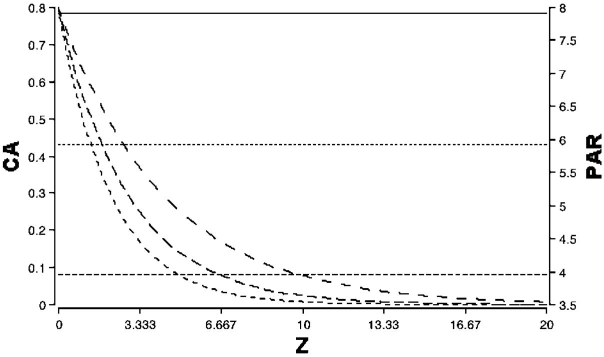


Fig. 2 These steady-state profiles were obtained from TUBE by setting three values of k.

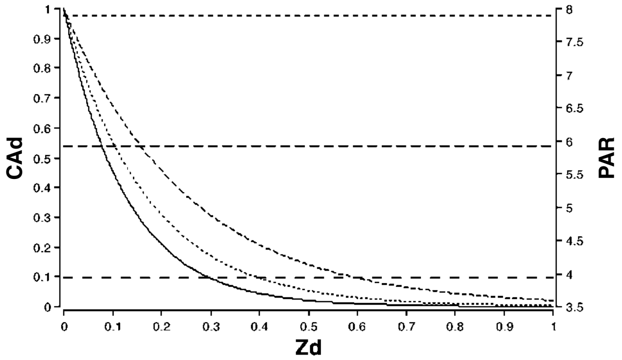


Fig. 3 These profiles were obtained from TUBEDIM by changing k as in Fig. 2, thus keeping the same values of PAR.

Reference

Levenspiel, O. (1999) Chemical Reaction Engineering, 3rd edition, Wiley.

5.4.2
TUBETANK – Design Comparison for Tubular and Tank Reactors

System

Steady-state conversions for both continuous tank and tubular reactors are compared for nth-order reaction kinetics.

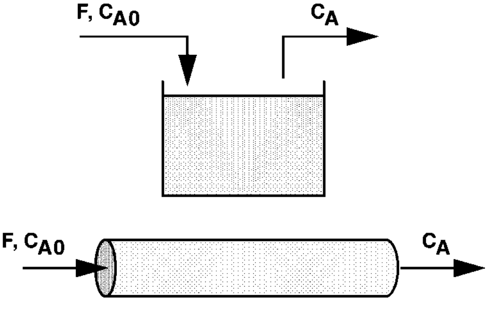


Fig. 1 Comparison of tank and tubular reactors.

The comparison is made by calculating the residence times and volumes required for a particular value of fraction conversion. This allows a comparison of the reactor volumes for a given flow rate. Levenspiel (1999) presents design graphs for the steady-state solution, similar to those generated by this program. One advantage of this method is an easy use of arbitrary kinetic functions.

Model

For a tank reactor with nth-order reaction at steady state

$$0 = FC_{A0} - FC_A - kC_A^n V$$

For n = 1

$$C_{ATa} = \frac{FC_{A0}}{F - kV} = \frac{C_{A0}}{1 - k\tau_{Ta}}$$

where τ_{Ta} is the mean residence time for the tank.

For a plug-flow tubular reactor with nth-order reaction at steady state

$$\frac{dC_A}{dZ} = \frac{-1}{v} kC_A^n$$

For n = 1

$$C_A = C_{A0} e^{-k\tau_{Tu}}$$

where the tubular reactor residence time τ_{Tu} is equal to Z/v.

For a given fraction conversion X_A, the residence time for n = 1 can be calculated from

$$\tau_{Tu} = \frac{1}{k} \ln \frac{1}{1 - X_A}$$

For nth-order reaction in terms of fraction conversion X_A for a tank

$$\tau_{Ta} kC_{A0}^{n-1} = \frac{X_A}{(1 - X_A)^n}$$

and for a plug-flow tubular reactor ($n \neq 1$) the integration gives

$$\tau_{Tu} kC_{A0}^{n-1} = \frac{-1}{1 - n} \left((1 - X_A)^{1-n} - 1 \right)$$

Program

The problem is not one that would normally be solved with a program such as MADONNA. The values for X_A generated from an integration are used to calculate quasi backwards the residence time and the volume required from the analytical steady state solutions for tubular and tank reactors. The STOPTIME is renamed XaStop.

Nomenclature

Symbols

C_A	Concentration of A	kg/m^3
F	Flow rate	m^3/s
k	Reaction rate constant	$m^{3(n-1)}/kg^{(n-1)}\ s$
n and n_0	Reaction order	
v	Flow velocity	m/s
V	Volume	m^3
V_{tuta}	Volume ratio, tube to tank	–
X_A	Fraction conversion	–
Z	Length variable	m
τ	Residence time	s

Indices

tu	Refers to tube
ta	Refers to tank
0	Refers to inlet conditions

Exercises

1. Set the volumetric flow rate and feed concentration for the tank and tubular reactors to desired values. Set also the order of reaction to $n=1.01$. Run for a range of fraction conversions from 0 to 0.99. Compare the required volumes for the two reactor types.
2. Rerun Exercise 1 for $n=2$ and compare the ratio of volumes V_{tuta}. Compare the required volumes for the two reactor types. Suppose a conversion of 90% is desired and the flow rate to the tank reactor is to be one-half that of the tubular reactor. What would be the ratio of volumes?
3. Repeat Exercise 2 with a 2-fold increase in C_{A0}. How do the required volumes compare. Repeat for $n=1.01$. Explain the results.
4. Use a dynamic model for a tank reactor to verify the values calculated by this program. Do the same for a steady state and dynamic tubular reactor model.

Results

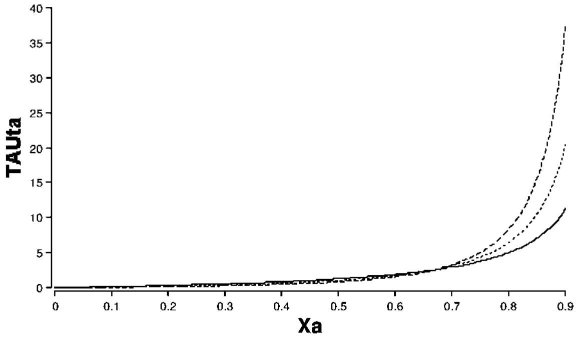


Fig. 2 The required volume for a tank reactor for reaction order n=1, 1.5, and 2.0 is plotted versus fraction conversion.

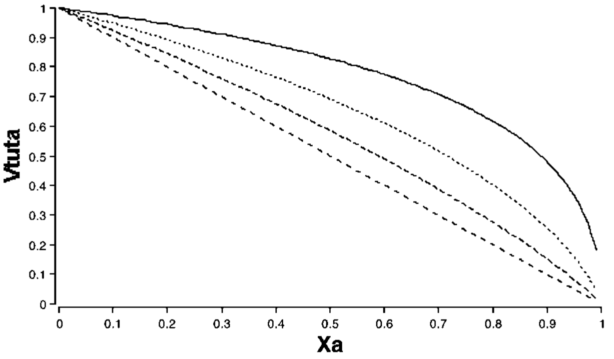


Fig. 3 The ratio of required residence times, tube to tank, is plotted versus conversion for reaction orders n=0.5, 1, 1.5, and 2.0:

Reference

Levenspiel, O. (1972) Chemical Reaction Engineering, 3rd edition, Wiley.

5.4.3
BENZHYD – Dehydrogenation of Benzene

System

The gas-phase dehydrogenation of benzene to diphenyl (D) and further to triphenyl (T) is conducted in an ideal isothermal tubular reactor. The aim is to maximize the production of D and to minimize the formation of T. Two parallel gas-phase reactions occur at atmospheric pressure.

Check these equations

$$2C_6H_6(B) \xrightarrow{k_1} C_{12}H_{10}(D) + H_2(H)$$

$$C_6H_6(B) + C_{12}H_{10}(D) \xrightarrow{k_2} C_{18}H_{14}(T) + H_2(H)$$

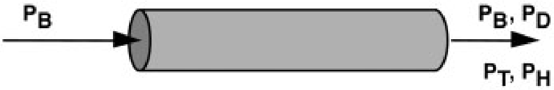


Fig. 1 The partial-pressure variables for the tubular reactor are shown.

Model

The kinetic model is given in terms of Arrhenius relationships and partial-pressure relationships as

$$r_1 = -k_1\left(P_B^2 - \frac{P_D P_H}{K_{eq1}}\right)$$

where

$$k_1 = 1.496E + 7 * \exp\left(\frac{8440}{T_r}\right)$$

$$r_2 = -k_2\left(P_B P_H - \frac{P_T P_H}{K_{eq2}}\right)$$

where

$$k_2 = 8.67E + 6 * \exp\left(\frac{8440}{T_r}\right)$$

At steady-state conditions, the mass balance design equations for the ideal tubular reactor apply. These equations may be expressed as

$$\frac{V}{F} = -\int \frac{dX_1}{r_1} = \tau$$

$$\frac{V}{F} = -\int \frac{dX_2}{r_2} = \tau$$

where X_1 is the fractional conversion of benzene by reaction 1, X_2 is the fractional conversion of benzene by reaction 2 and τ is the reactor space time.

In differential form

$$\frac{dX_1}{d\tau} = -r_1$$

$$\frac{dX_2}{d\tau} = -r_2$$

Expressing P_B, P_D, P_H and P_T in terms of X_1 and X_2.

$$P_B = (1 - X_1 - X_2)$$

$$P_D = \frac{X_1}{2} - X_2$$

$$P_H = \frac{X_1}{2} + X_2$$

$$P_T = X_2$$

Substituting into the mass balance

$$\frac{dX_1}{d\tau} = k_1\left((1 - X_1 - X_2)^2 - \frac{\left(\frac{X_1}{2} - X_2\right)\left(\frac{X_1}{2} + X_2\right)}{K_{eq1}}\right)$$

$$\frac{dX_2}{d\tau} = k_2\left((1 - X_1 - X_2)\left(\frac{X_1}{2} - X_2\right) - \frac{X_2\left(\frac{X_1}{2} + X_2\right)}{K_{eq2}}\right)$$

Nomenclature

Symbols

k_{eq1}, k_{eq2}	Equilibrium constants	–
k_1, k_2	Reaction rate constants	$1/atm^2$ h
P_B	Partial pressure of benzene	atm
P_D	Partial pressure of diphenyl	atm
P_H	Partial pressure of hydrogen	atm
P_T	Partial pressure of triphenyl	atm
r_1 and r_2	Reaction rates	1/h
Tr	Temperature	K
X_1 and X_2	Fractional conversion	–
τ	Space time	h

Exercises

1. Study the effect of varying space time on the fractional conversions X1 and X2 and evaluate the compositions of benzene, hydrogen, diphenyl and triphenyl.
2. Show that the diphenyl composition passes through a maximum.
3. Study the effect of varying pressure on the reaction by modifying the partial-pressure relationships.
4. Plot the rates r_1 and r_2 as functions of space time.
5. Study the effects of temperature.

Results

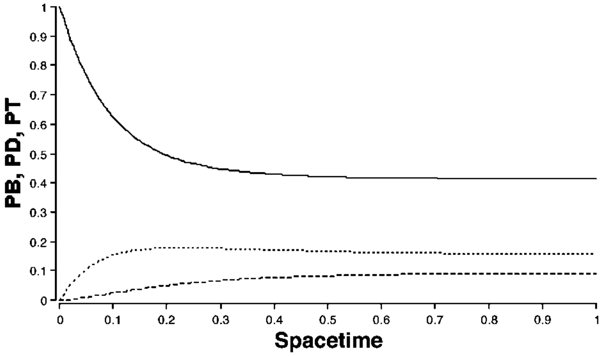


Fig. 2 A maximum in the diphenyl (PD) composition is obtained.

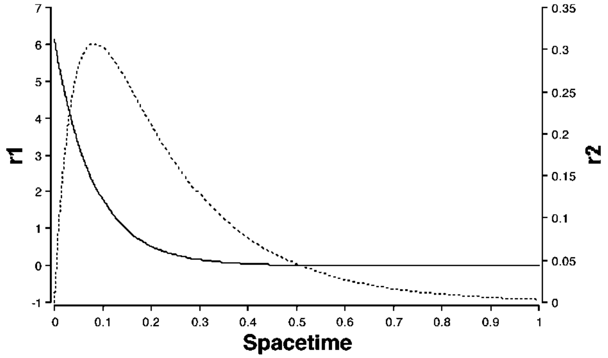


Fig. 3 The reaction rate of the second reaction step exhibits a maximum as a function of reactor space-time.

Reference

Smith, J. M. (1970) Chemical Engineering Kinetics, 2nd edition, p. 158, McGraw-Hill.

5.4.4
ANHYD – Oxidation of O-Xylene to Phthalic Anhydride

System

Ortho-xylene (A) is oxidised to phthalic anhydride (B) in an ideal, continuous flow tubular reactor. The reaction proceeds via the complex consecutive parallel reaction sequence, shown below. The aim of the reaction is to produce the maximum yield of phthalic anhydride and the minimum production of waste gaseous products (C), which are CO_2 and CO.

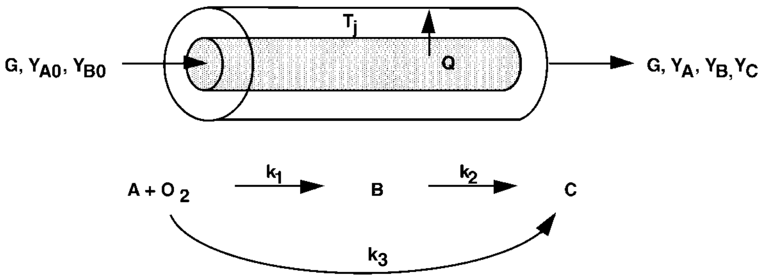


Fig. 1 The fixed-bed reactor and the reaction scheme.
Symbols: A = o-xylene, B = phthalic anhydride, C = waste gaseous products (CO_2 and CO).

The reaction is carried out with a large excess of air, and the total gas mass flow rate can be taken as constant.

Froment and Bischoff (1990) have discussed the modelling of the fixed bed production of phthalic anhydride from o-xylene, including both axial and radial temperature profile effects.

Model

Kinetics

The reaction kinetics is as follows

$$r_A = -(k_1 + k_3) Y_A Y_{O_2}$$

$$r_B = k_1 Y_A Y_{O_2} - k_2 Y_B Y_{O_2}$$

$$r_C = k_3 Y_A Y_{O_2} + k_2 Y_B Y_{O_2}$$

It is assumed that the mole fraction of oxygen does not change, owing to the large excess of air.

The temperature dependencies are according to Arrhenius

$$\ln k_1 = -\frac{27000}{RT} + 19.837$$

$$\ln k_2 = -\frac{31400}{RT} + 20.86$$

$$\ln k_3 = -\frac{28600}{RT} + 18.97$$

Component Mass Balance Equations

Considering Fig. 2, the steady-state balance around any segment ΔV, for component A, is given by

$$0 = n_{AF} - (n_{AF} + \Delta n_{AF}) + r_A \rho \Delta V$$

where n_{AF} is the molar flow rate of A in kmol/h and F_m is the mass flow rate in kg/h (=GA_c).

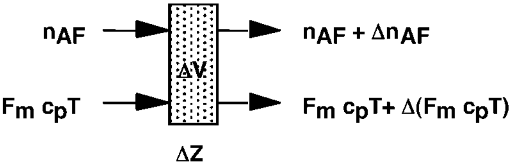


Fig. 2 The balance region ΔV.

Thus the changes in the molar flow rates (kmol/hm) at steady state can be set equal to the rates of production of each component.

$$\frac{dn_{AF}}{dZ} = A_c \rho r_A$$

$$\frac{dn_{BF}}{dZ} = A_c \rho r_B$$

$$\frac{dn_{CF}}{dZ} = A_c \rho r_C$$

The cross-sectional area of the reactor is given by

$$A_c = \pi \frac{d_t^2}{4}$$

The total molar flow (mostly air) does not change. Thus

$$n_{tF} = \frac{G}{M_m} A_c$$

The mole fractions can be calculated by

$$Y_A = \frac{n_{AF}}{n_{tF}}$$

$$Y_B = \frac{n_{BF}}{n_{tF}}$$

$$Y_C = \frac{n_{CF}}{n_{tF}}$$

The fractional conversions of A to B and C are given by

$$X_A = \frac{n_{AF0} - n_{AF}}{n_{AF0}}$$

$$X_B = \frac{n_{FB}}{n_{AF0} - n_{AF}}$$

$$X_C = \frac{n_{FC}}{n_{AF0} - n_{AF}}$$

Energy Balance

At steady state the energy balance for element ΔV is

$$0 = -\Delta(F_m c_p T) + \rho \Delta V \Sigma(r_i \Delta H_i) - UA_t(T - T_j)$$

where the heat transfer area $A_t = \pi d_t \Delta Z$ and the element $\Delta V = A_c \Delta Z$. Thus

$$\frac{dT}{dZ} = \frac{\rho A_c}{F_m c_p}((\Delta H_1 k_1 + \Delta H_3 k_3) Y_A Y_{O2} + \Delta H_2 k_2 2 Y_A Y_{O2}) - \frac{U \pi d_t}{F_m c_p}(T - T_j)$$

The above equations are solved with the initial conditions at the reactor entrance given by

$$n_{AF} = Y_{A0} n_{tF}$$

$$n_{BF} = n_{CF} = 0$$

$$T = T_{in}$$

Program

The particle diameter (not used in the program) can be used to normalize the length Z. The factors 1000 on k_1, k_2 and k_3 in the program convert gmol to kmol.

Nomenclature

Symbols

A_c	Area cross-section	m^2
c_p	Specific heat	kJ/kg K
ΔH_1	Heat of reaction A → B	kJ/kmol
ΔH_3	Heat of reaction A → C	kJ/kmol
d_t	Tube diameter	m
E	Activation energy of reaction	kJ/kmol
F_m	Mass flow rate	kg/h
G	Superficial mass velocity	kg/m^2 h
k	Rate constant	kmol/(kg cat.) h
M_m	Mean molecular weight	kg/gmol
n	Molar flow rate	kmol/h
nAF	Molar flow rate of A	kmol/h
nBF	Molar flow rate of B	kmol/h
nCF	Molar flow rate of C	kmol/h
ntF	Total molar flow rate	kmol/h
R	Universal gas constant	kJ/kmol K
ρ	Catalyst bulk density	kg/m^3
r	Reaction rate	kmol/(kg cat.) h
T and Temp	Temperature	K
U	Heat transfer coefficient	kJ/m^2 h K
V	Volume	m^3
Y	Mole fraction	–
Z	Distance along tube	m

Indices

A, B, C, O_2	Refer to components
F	Refers to flow
j	Refers to jacket
t	Refers to total
1, 2, 3	Refer to reactions
0	Refers to inlet

Exercises

1. Study the effect of tube diameter on the axial profiles.
2. Study the effect of inlet temperature with constant jacket temperature. Note the hot spot effect in the reactor temperature profile.
3. Study the effect of jacket temperature on the temperature profile, by keeping T_0 constant and varying T_j.

4. Repeat Exercise 1 and 2 setting $k_3 = 0$. Observe that the reaction rate A to C is relatively small but has a large influence on the temperature of the reactor.

Results

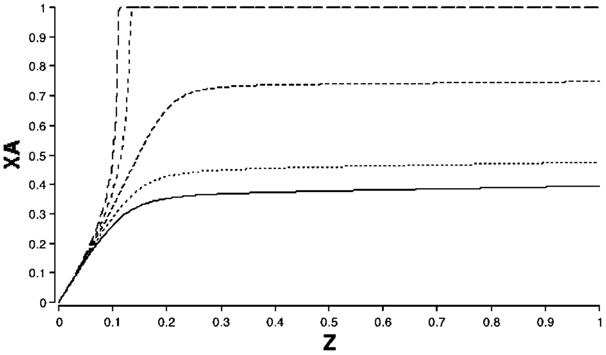


Fig. 3 The influence of jacket temperature ($T_J = 580$ to 590 K) is seen in these steady-state conversion profiles.

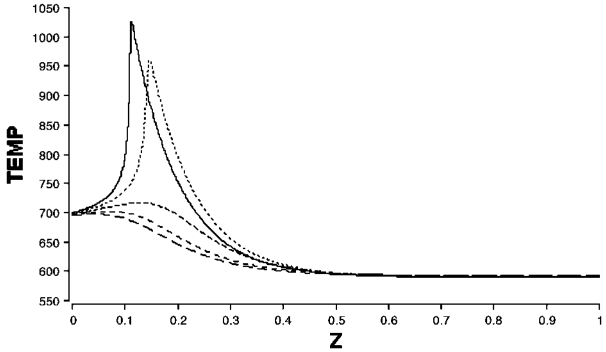


Fig. 4 The temperature profiles are strongly influenced by the feed temperature 695 to 700 K.

Reference

Froment, G. E., Bischoff, K. B. (1990) Chemical Reactor Analysis and Design, 2nd edition, Wiley.

5.4.5
NITRO – Conversion of Nitrobenzene to Aniline

System

Nitrobenzene and hydrogen are fed at the rate of n_{tF} to a tubular reactor operating at atmospheric pressure and 450 K and containing catalyst with a voidage ε.

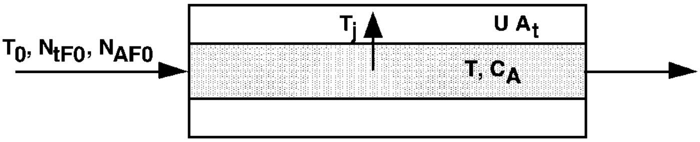


Fig. 1 Tubular reactor with heat transfer.

The heat transfer coefficient, U, to the reactor wall and the coolant temperature is T_j. The nitrobenzene feed rate is N_{AF0}, with hydrogen in very large excess. The heat of reaction is ΔH. The heat capacity of hydrogen is c_p.

The reaction rate is given by

$$r_A = -5.79 \times 10^4 C_A^{0.578} e^{-2958/T}$$

where r_A has the units of kmoles (of nitrobenzene reacting)/(m^3 of void space h) and C_A is the concentration of nitrobenzene (kmol/m^3). This problem is considered in many chemical engineering texts, but here the solution by digital simulation is shown to be very convenient.

Model

Mass Balance

Consider the steady state balances around the segment ΔV, as shown in Fig. 2

$$0 = N_{AF} - (N_{AF} + \Delta N_{AF}) + r_A \rho \Delta V$$

where N_{AF} is the molar flow rate of A (kmol/h).

$$0 = (N_{tF} c_p T) - (N_{tF} c_p T + \Delta(N_{tF} c_p T)) + r_A \Delta V \Delta H - U A_t (T - T_j)$$

where N_{tF} is the total molar flow rate (kmol/h), which can be assumed constant owing to the large excess of hydrogen in the feed.

The changes in the molar flowrate of A with distance Z at steady-state conditions are thus

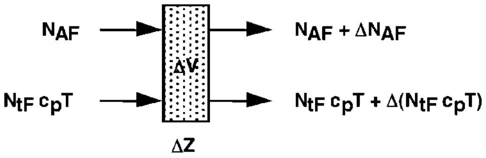


Fig. 2 Balance region for a segment.

$$\frac{dN_{AF}}{dZ} = A_c r_A$$

where

$$A_c = \pi \frac{d_t^2}{4} \varepsilon$$

The fractional conversion of A is

$$X_A = \frac{N_{AF0} - N_{AF}}{N_{AF0}}$$

and

$$dN_{AF} = -N_{AF0} dX_A$$

The balance becomes

$$\frac{dX_A}{dZ} = -\frac{A_c}{N_{AF0}} r_A$$

Energy Balance

At steady-state for constant N_{tF} and c_p

$$0 = -N_{tF}c_p\Delta T + \Delta V r_A \Delta H - UA_t(T - T_j)$$

where the transfer area $A_t = \pi d_t \Delta Z$ and the volume element $\Delta V = A_c \Delta Z$.

Thus

$$\frac{dT}{dZ} = \frac{A_c}{N_{tF}c_p}\Delta H r_A - \frac{U\pi d_t}{N_{tF}c_p}(T - T_j)$$

Kinetics

The reaction rate is

$$r_A = -5.79 \times 10^4 C_A^{0.578} e^{-2958/T}$$

where

$$C_A = C_{A0}(1 - X_A)\frac{T_0}{T} = (1 - X_A)\frac{N_{AF0}}{N_{tF}}\frac{P_{tot}}{RT}$$

The above equations are solved with the initial conditions at the reactor entrance

$$X_A = 0 \quad \text{and} \quad T = T_{in}$$

Nomenclature

Symbols

A_c	Cross-sectional area for flow	m^2
A_t	Transfer area of tube	m^2
C_A	Concentration of nitrobenzene	$kmol/m^3$
c_p	Heat capacity of hydrogen	kJ/kmol K
ΔH	Heat of reaction	kJ/kmol
d_t	Diameter of tube	m
ε	Catalyst with voidage	–
N_{AF}	Nitrobenzene molar flow rate	kmol/h
N_{tF}	Total molar flow rate	kmol/h
P_{tot}	Total pressure	atm
R	Gas constant	m^3 atm/kmol K
r_A	Reaction rate	$kmol/m^3$ voids h
T and Temp	Reactor temperature	K
T_j	Coolant temperature	K
U	Heat transfer coefficient	kJ/h m^2 K
X	Fraction conversion	–
Z	Reactor length	m

Indices

0	Refers to entering conditions

Exercises

1. Run the program for varying inlet temperatures 350 to 500 K.
2. Study also the effect of coolant temperature.
3. Comment on the monotonously decreasing temperature profiles in the last part of the reactor.
4. Modify the program such that it models adiabatic behaviour and study the influence of varying feed temperature.

Results

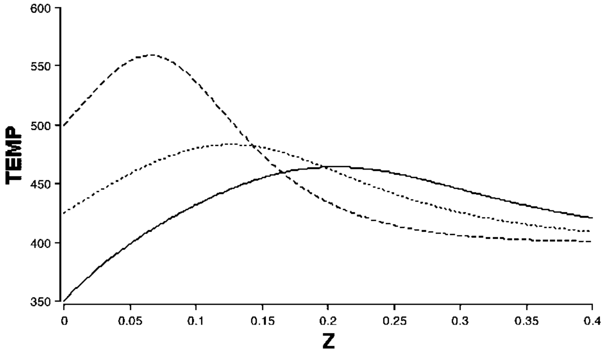


Fig. 3 The inlet temperatures were set at 350, 425 and 500 for these axial temperature profiles.

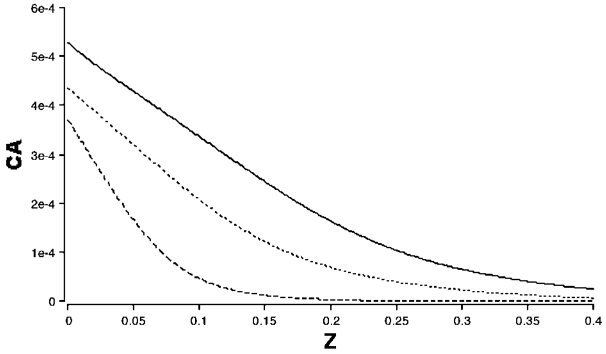


Fig. 4 The reactor concentrations for the conditions of Fig. 3. Note that the inlet concentrations depend on inlet temperature.

Reference

Smith, J.M. (1972) Chemical Engineering Kinetics, 2nd edition, McGraw-Hill.

5.4.6
TUBDYN – Dynamic Tubular Reactor

System

Tanks-in-series reactor configurations provide a means of approaching the conversion of a tubular reactor. In modelling, systems of tanks in series are employed for describing axial mixing in non-ideal tubular reactors. Residence time distributions, as measured by tracers, can be used to characterise reactors, to establish models and to calculate conversions for first-order reactions. The reactor in this example has a recycle loop to provide additional flexibility in modelling the mixing characteristics.

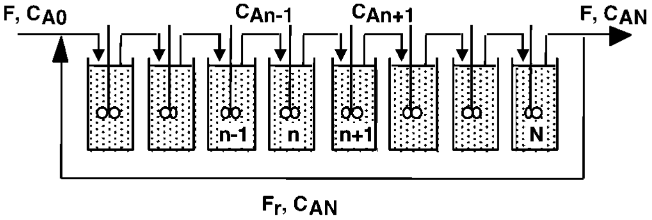


Fig. 1 Tanks-in-series approximation of a tubular reactor with recycle.

Model

For the nth tank the balance for a single component is

$$V\frac{dC_{An}}{dt} = (F + F_r)(C_{An-1} - C_{An}) + r_{An}V$$

If applied to a tracer, r_{An} is zero. Otherwise the reaction rate is taken as nth-order

$$r_{An} = kC^{n,An}$$

Residence time distributions can be measured by applying tracer pulses and step changes and, as described in Levenspiel (1999), the pulse tracer response can be used to obtain the E-curve and to calculate the steady-state conversion for a first-order reaction according to the relationship

$$\frac{C_{Ass}}{C_{A0}} = \int_0^{\infty} E(t)e^{-kt}dt$$

Program

This program is designed to simulate the resulting residence time distributions based on a cascade of 1 to N tanks-in-series. Also, simulations with nth-order reaction can be run and the steady-state conversion obtained. A pulse input disturbance of tracer is programmed here, as in example CSTRPULSE, to obtain the residence time distribution E curve and from this the conversion for first order reaction.

Nomenclature

Symbols

C_{A0}	Feed reactant concentration	kg/m^3
C_{AN}	Concentration in tank N	kg/m^3
F	Flow rate	m^3/s
k	Reaction constant	various
n	Reaction order	–
N	Number of tanks	–
R	Reaction rate	$kg/m^3\ s$
V	Total volume of all tanks	m^3

Indices

n	Refers to nth tank
r	Refers to recycle
t	Refers to time
ss	Refers to steady-state

Exercises

1. Set $k=0$ and simulate tracer experiments. Vary the recycle flow rate and the number of tanks.
2. Use the E-curve to calculate the conversion for $n=1$ and compare with the results obtained by simulation. This requires changing the program.
3. Vary the operating variables of feed flow rate and C_{A0} to see the influence with $n=1$ and $n=2$.
4. Calculate the steady-state conversion for 1, 3 and 8 tanks using the same value of total residence time.
5. Experiment with the influence of recycle flow rate and show by simulation that the model has the limits of a well-stirred tank and a plug flow reactor.

Results

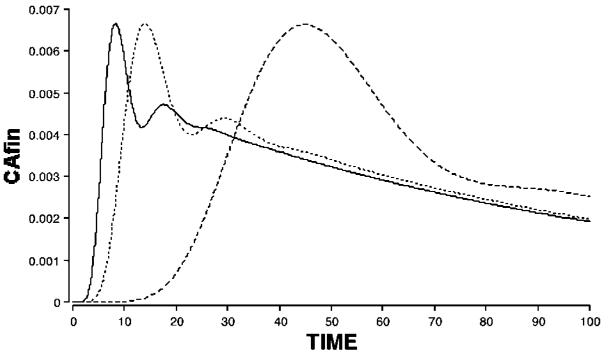


Fig. 2 Pulse response curves for tracer at 3 recycle rates $F_r=1$, 5.5 and 10.

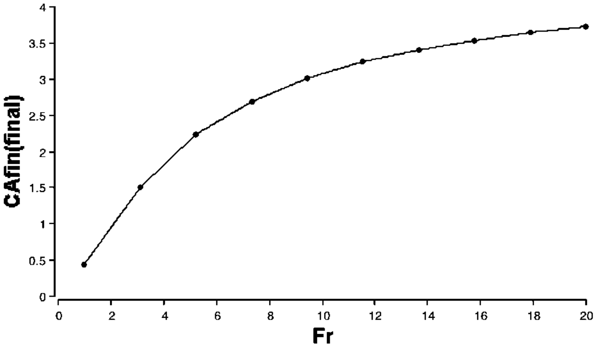


Fig. 3 Steady state outlet concentrations for first order reaction as a function of recycle rate.

Reference

Levenspiel O. (1999) Chemical Reaction Engineering, 3rd edition, Wiley.

5.4.7
DISRE – Isothermal Reactor with Axial Dispersion

System

This example models the dynamic behaviour of an non-ideal isothermal tubular reactor in order to predict the variation of concentration, with respect to both axial distance along the reactor and flow time. Non-ideal flow in the reactor is represented by the axial dispersion flow model. The analysis is based on a simple, isothermal first-order reaction.

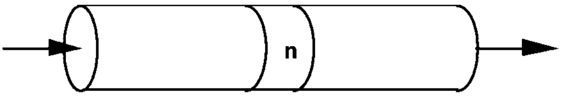


Fig. 1 Tubular reactor with finite-difference element n.

Model

The reaction involves the conversion: A → products, with the kinetics

$$-r_A = kC_A$$

As discussed in Section 4.3.6, the axial dispersion flow model is given by

$$\frac{\partial C_A}{\partial t} = -u\frac{\partial C_A}{\partial Z} + D\frac{\partial^2 C_A}{\partial Z^2} - kC_A$$

where Z is the distance along the reactor, D is the eddy diffusivity and u is the superficial flow velocity.

Thus the problem involves the two independent variables, time t and length Z. The distance variable can be eliminated by finite-differencing the reactor length into N equal-sized segments of length ΔZ, such that $N\Delta Z$ equals L, where L is the total reactor length.

Thus for a segment n omitting subscripts A

$$\frac{dC_n}{dt} = u\left(\frac{C_{n-1} - C_n}{\Delta Z}\right) + D\left(\frac{C_{n-1} - 2C_n + C_{n+1}}{\Delta Z^2}\right) - kC_n$$

Or defining $C'_n = C_n/C_0$, $\Delta z = \Delta Z/L$, $\Theta = tu/L$ in dimensionless terms and omitting the primes for simplicity

$$\frac{dC_n}{d\Theta} = \frac{C_{n-1} - C_n}{\Delta z} + \frac{D}{Lu}\left(\frac{C_{n-1} - 2C_n + C_{n+1}}{\Delta z^2}\right) - \frac{kL}{u}C_n$$

The term Lu/D is known as the Peclet number, Pe, and its inverse as the dispersion number. The magnitude of the Peclet number defines the degree of axial mixing in the reactor.

Thus

$$\frac{dC_n}{d\Theta} = \frac{C_{n-1} - C_n}{\Delta z} + \frac{1}{Pe}\left(\frac{C_{n-1} - 2C_n + C_{n+1}}{\Delta z^2}\right) - \frac{kL}{u}C_n$$

The dimensionless boundary conditions are satisfied by $C_0 = 1$ for a step change in feed concentration at the inlet and by the condition that at the outlet

$C_{N+1} = C_N$, which sets the concentration gradient to zero. The reactor is divided into equal-sized segments.

Program

Array programming is used here which allows the graphing of the axial profile. Closed-end boundary conditions are used for the first and last segments. Also included is a PULSE function for simulating tracer experiments. Thus it should be possible to calculate the E curve and from that the reaction conversion obtained on the basis of tracer experiment. The example CSTRPULSE should be consulted for this.

The full listing of the MADONNA program is shown here both to illustrate the use of array programming and also the use of the PULSE function.

```
{Example DISRE}

{UNSTEADY-STATE FINITE-DIFFERENCED MODEL FOR AXIAL DISPER-
SION AND REACTION IN A TUBULAR REACTOR}
{The reactor length is divided into equal-sized sections,
whose number, Nelem, can be varied. The model equations are
written in dimensionless form.
{The variable Time is dimensionless and equal to tu/L.}
{The Peclet number is equal to Lu/D, where D is the axial dif-
fusivity.}
{All concentrations C[i] are dimensionless and equal to C/C0}

{From HELP: PULSE(v, f, r) Impulses of volume v, first time f,
repeat interval r}
{For the nonreacting system with K=0, making a pulse of tracer
at the inlet with C0=0 and measuring C[Nelem] at the outlet
gives information on the degree of axial mixing. This pulse is
programmed below and can be activated by removing the brack-
ets. This simulated measurement can be used to calculate the
steady state conversion for a first order reaction.}

Method Stiff
DT=0.001
STOPTIME=4

L=10                   {Total length, m }
U=1                    {Velocity, m/h}
C0=1                   {Entering dimensionless conc., -}
Pe=0.5                 {Peclet number=Lu/D, -}
K=0.01                 {Rate constant, 1/hr}
CI=0                   {Initial concentration conditions, -}
```

```
delZ = 1.0/Nelem       {Dimensionless length increment, -
                       Dimensionless length has a value of 1.0}

K1=K*L/U               {Dimensionless ratio of reaction rate
                       to convective transport rate}

Nelem=10               {Number of elements}
NIT C[1..Nelem-1]=CI   {Initial concentrations, -}

{Dimensionless reactant balances for Nelem sections, with
"closed-end" boundary conditions}
d/dt(C[1])=(C0-C[1])/delZ-(C[1]
C[2])/(delZ*delZ*Pe)-K1*C[1]

d/dt(C[2..Nelem-1])=(C[i-1]-C[i])/delZ+(C[i-1]-
2*C[i]+C[i+1])/(delZ*delZ*Pe)-K1*C[i]

d/dt(C[Nelem])=(C[Nelem-1]-C[Nelem])/delZ+(C[Nelem-1]-
C[Nelem])/(delZ*delZ*Pe)-K1*C[Nelem]

LIMIT C>=0

{Brackets can be set or removed for the pulse of tracer. Set
K=0 to make a tracer experiment with no reaction.}
C0=Pulse(0.01, starttime, 1000)
Cpulse=C[Nelem] {This is the outlet conc. for the pulse}
```

Nomenclature

Symbols

C	Concentration	kmol/m^3 and –
D	Effective axial diffusivity	m^2/h
k	Rate constant	1/h
L	Total length	m
Pe	Peclet number (Lu/D)	–
t	Time	h
u	Velocity	m/h
Z	Length variable	m
z	Dimensionless length	–
Θ	Dimensionless time	–

Indices

A	Refers to reactant
n	Refers to increment number
′	Refers to a dimensionless variable

Exercises

1. Obtain the tracer response curve to a step input disturbance of tracer solution by setting k=0.
2. Study the effect of varying Peclet number, Pe, on the resulting tracer response.
3. Note that as Pe becomes large, the conditions approach plug flow, and as Pe approaches zero conditions approach perfect mixing.
4. Study the effect of varying Pe on the performance of the reactor, and compare the resulting performance with perfect plug flow.
5. Use the E curve from a pulse tracer experiment to calculate the first-order conversion.

Results

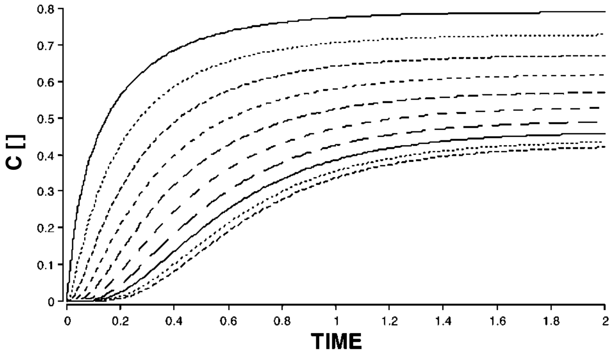


Fig. 2 Dynamic concentration profiles at each axial position in the reactor for a first order reaction.

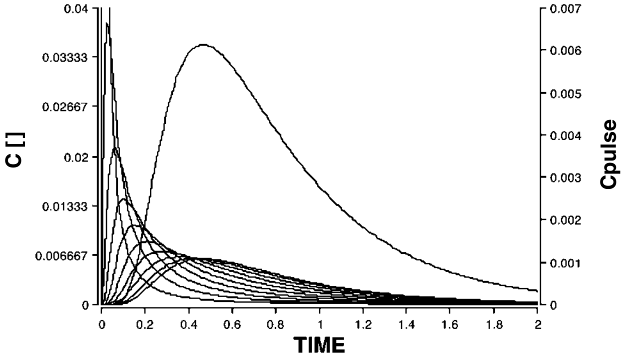


Fig. 3 Response of reactor to a pulse input of tracer. The outlet concentration from the last element is graphed separately.

5.4.8
DISRET – Non-Isothermal Tubular Reactor with Axial Dispersion

System

The dispersion model of example DISRE is extended for the case of non-isothermal reactions and to include the axial dispersion of heat from a first-order reaction.

$$A \rightarrow B + \text{heat}(-\Delta H)$$

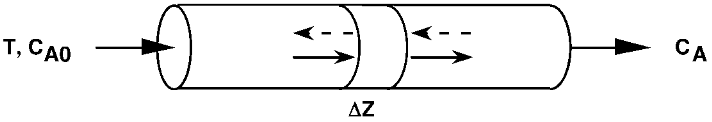


Fig. 1 Tubular reactor showing a finite difference segment.

Model

From the axial dispersion flow model the component balance equation is

$$\frac{\partial C_A}{\partial t} = -u\frac{\partial C_A}{\partial z} + D\frac{\partial^2 C_A}{\partial^2 z} - kC_A$$

with the energy balance equation given by

$$\rho c_p \frac{\partial T}{\partial t} = -c_p u\frac{\partial T}{\partial z} + \lambda\frac{\partial^2 T}{\partial z^2} - kC_A(-\Delta H)$$

where λ is the eddy diffusivity for heat transfer.

The reaction kinetics are

$$r_A = kC_A$$

and

$$k = k_0 e^{-E/RT}$$

Defining $Z=z/L$, $t=T/T_0$, $C=C_A/C_{A0}$, $\Theta=Dt/L^2$, the model equations can be recast into dimensionless terms to give the following dimensionless model equations:

Mass Balance

$$\frac{\partial C}{\partial \Theta} = \frac{\partial^2 C}{\partial Z^2} - P_1\frac{\partial C}{\partial Z} - B_1 C e^{-\varepsilon/t}$$

Energy Balance

$$\frac{\partial t}{\partial \Theta} = \frac{\alpha}{D}\frac{\partial^2 t}{\partial Z^2} - P_2\frac{\partial t}{\partial Z} - B_1 B_2 C e^{-\varepsilon/t}$$

where

$$P_1 = \frac{uL}{D}, \quad P_2 = \frac{uL}{\alpha}, \quad \alpha = \frac{\lambda}{\rho c_p}, \quad B_1 = \frac{k_0 L^2}{D}, \quad B_2 = (-\Delta H)\frac{C_{A0}}{\rho c_p T_0}$$

and $\varepsilon = \dfrac{E}{RT_0}$

A full treatment of this problem is given by Ramirez (1976, 1989) and by Clough and Ramirez (1971).

Finite-differencing the dimensionless length of the reactor ($Z=1$) into N equal-sized segments of length ΔZ, such that $N\,\Delta Z = L$, gives for segment n

$$\frac{dC_n}{d\Theta} = \frac{C_{n-1} - 2C_n + C_{n+1}}{\Delta Z^2} + P_1\frac{C_{n-1} - C_n}{\Delta Z} - B_1 C_n e^{\varepsilon/t_n}$$

and

$$\frac{dt_n}{d\Theta} = \frac{\alpha}{D}\frac{t_{n-1} - 2t_n + t_{n+1}}{\Delta Z^2} + P_2\frac{t_{n-1} - t_n}{\Delta Z} - B_1 B_2 C_n e^{-\varepsilon/t_n}$$

The boundary conditions used here are $C_0 = t_0 = 1$ for a step change of inlet concentration or temperature, and at the outlet by $t_{N+1} = t_N$ and $C_{N+1} = C_N$.

Program

Array programming is used, which allows the graphing of the axial profiles. Closed-end boundary conditions are used for the first and last segments.

PULSE functions could be used for studying the axial dispersion of heat or, alternatively, the axial dispersion of mass (see DISRE).

Nomenclature

Symbols

C_A	Concentration	kmol/m^3
C_{A0}	Inlet concentration	kmol/m^3
c_p	Specific heat	kJ/kg K
D	Mass transfer eddy diffusiviy	m^2/s
ΔZ	Dimensionless length increment	–

E	Activation energy	kJ/kmol
(–ΔH)	Heat of reaction	kJ/kmol
L	Reactor length	m
λ	Heat transfer eddy diffusivity	kJ/m s K
R	Universal gas constant	kJ/kmol K
r_A	Reaction rate	kmol/m^3 s
ρ	Density	kg/m^3
t	Time	s
T_0	Inlet temperature	K
u	Flow velocity	m/s
Z	Frequency factor	1/s
α	Diffusivity of heat	m^2/s

Dimensionless Factors

B_1	Dimensionless group	–
B_2	Dimensionless group	–
C	Dimensionless concentration	–
P_1	Peclet number for mass transfer	–
P_2	Peclet number for heat transfer	–
t	Dimensionless temperature	–
Z	Dimensionless length	–
ε	Activation energy group	–
Θ	Dimensionless time	–

Exercises

1. Setting B_1, and hence $k_0=0$, models the reactor response curve to a step input disturbance $C_{A0}=1$.
2. Vary reactor inlet temperature up to 700 K.
3. Study the effect of varying mass transfer and heat transfer diffusivities (D and λ, respectively) and hence Peclet numbers (P_1 and P_2) on the resulting dimensionless concentration and temperature reactor profiles.
4. Based on a linearisation approach as applied to the nonlinear model equations, Clough and Ramirez (1971) predict multiple, steady-state solutions for the reactor. Is this confirmed and if not, why not?
5. Verify that the unusual mixed units used here actually give the dimenionless groups as stated and that the dimensionless balances are consistent.
6. Revise the model to allow for open-end boundary conditions. This would be the case if the reactor were a catalytic packed bed with non-catalytic packing beyond the reactor ends (Fig. 2).

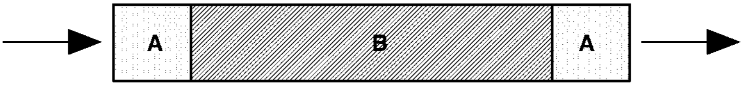


Fig. 2 Catalytic packed bed reactor with non-reactive end sections.

Results

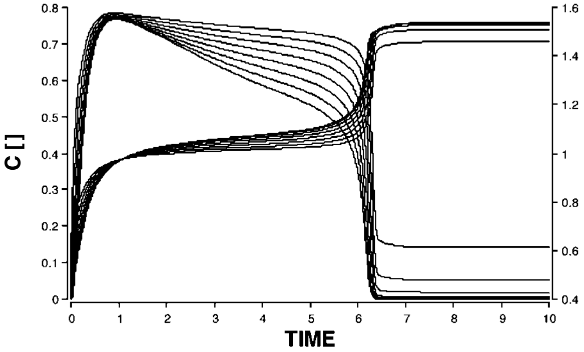


Fig. 3 The reactor responding in C and T for each segment before reaching steady state.

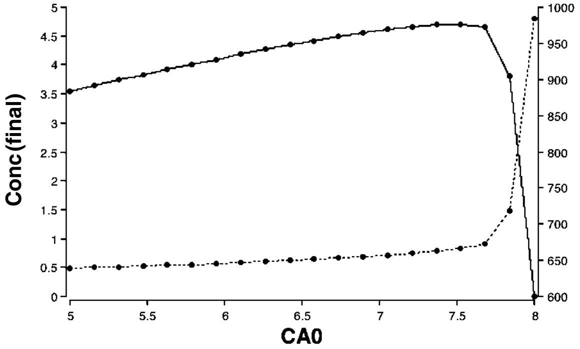


Fig. 4 Steady states for C and T as a parametric run varying inlet concentration.

References

Clough, D.E. and Ramirez, W.F. (1971) Simulation, 207.
Ramirez, W.F. (1976) Process Simulation, Lexington.

5.4.9

VARMOL – Gas-Phase Reaction with Molar Change

System

A tubular reactor is considered in which the gas-phase reaction leads to a change in the molar flow rate and thus in the linear gas velocity. The reaction stoichiometry is represented by

$$A \rightarrow mB$$

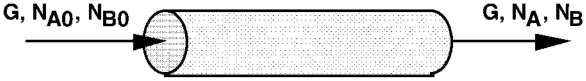


Fig. 1 Tubular reactor with variable molar flow.

Model

The model is described in Section 4.3.3. The steady-state balances are written in terms of moles. From the molar flow at each point in the reactor, the Ideal Gas Law is used to calculate the volumetric flow rate. This gives also the possibility of considering the influence of temperature and pressure profiles along the tube:

$$\frac{d(y_A G)}{dZ} = -k y_A A$$

$$\frac{d(y_B G)}{dZ} = +m k y_A A$$

$$G = \frac{(N_A + N_B + N_{inerts})}{P}$$

$$N_A = \frac{y_A G P}{RT}$$

$$N_B = \frac{y_B G P}{RT}$$

Nomenclature

Symbols

A	Cross-sectional area	m^2
G	Volumetric flow rate	m^3/s
k	Reaction rate	$1/s$

m	Stoichiometric constant	–
N	Molar flow rate	kmol/s
P	Pressure	N/m^2
R	Gas constant	kJ/kmol K
Temp	Temperature	K
X_A	Fraction conversion	–
y	Mole fraction	–
Z	Length	m

Indices

0	Refers to inlet
inerts	Refers to inerts
A	Refers to component A
B	Refers to component B

Exercises

1. Vary the stoichiometry to see the influence of m. Note that if m=1, G must be constant through the reactor.
2. Set the molar feed rate of inerts to a high value, and note that G does not change much with position.
3. Change the model and program to account for a linear temperature profile.
4. Change the model and program to account for a linear pressure profile, allowing for pressure drop through the reactor.

Results

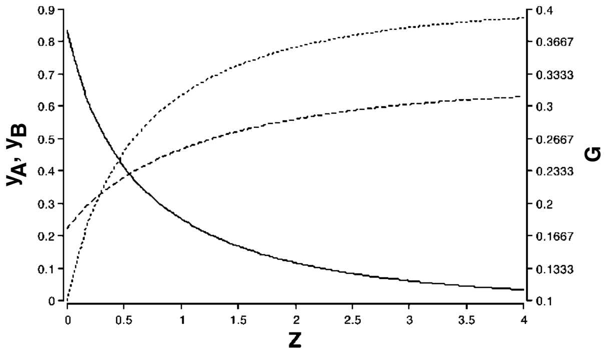


Fig. 2 Variation of mole fractions y_A and y_B and volumetric flow rate G with length.

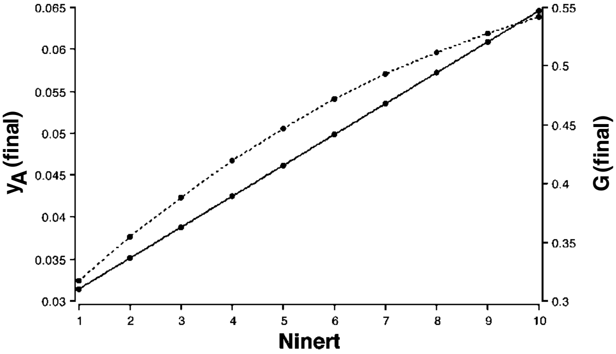


Fig. 3 Outlet mole fraction y_A as a function of molar flow rate of inerts.

5.5
Semi-Continuous Reactor Examples

5.5.1
SEMIPAR – Parallel Reactions in a Semi-Continuous Reactor

System

A semi-continuous reactor is used to carry out the following parallel reaction, where P is valuable product and Q is unwanted waste. The problem is to optimise the feed strategy to the reactor such that the maximum favourable reaction selectivity is obtained, for similar systems but of differing kinetic rate characteristics.

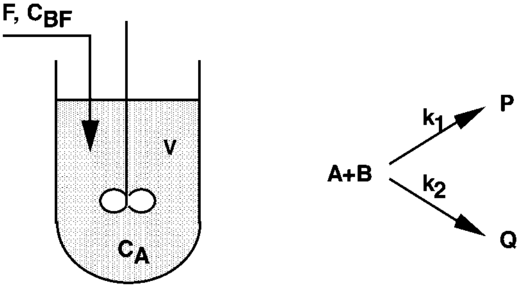


Fig. 1 Parallel reactions in a semi-continuous reactor.

Model

The total mass balance for constant density is

$$\frac{dV}{dt} = F$$

The mass balances for components A, B, P and Q are

$$\frac{d(VC_A)}{dt} = -(r_1V + r_2V)$$

$$\frac{d(VC_B)}{dt} = F\,C_{BF} - (r_1V + r_2V)$$

$$\frac{d(VC_P)}{dt} = r_1\,V$$

$$\frac{d(VC_Q)}{dt} = r_2V$$

The kinetics for the parallel reactions are

$$r_1 = k_1 C_A^{n_{A1}} C_B^{n_{B1}}$$

$$r_2 = k_2 C_A^{n_{A2}} C_B^{n_{B2}}$$

The relative magnitudes of the orders of reaction, n_{B1} and n_{B2}, determine whether the concentration C_B in the reactor should be maintained at a high or low level. For optimum selectivity, the total reaction time must be adjusted such that P is obtained at its maximum concentration as affected by the rate at which B is fed to the reactor.

Program

Note that, at high rates of feeding, the maximum reactor volume may be reached before the simulation time is complete. Under these conditions, the feed of B to the reactor will stop. The reaction then continues batchwise until the simulation is complete.

Nomenclature

Symbols

C	Concentration	$kmol/m^3$
V	Volume	m^3
F	Flow rate	m^3/min
r	Reaction rate	$kmol/m^3 min$

Indices

A, B, P, Q	Refer to components
F	Refers to inlet feed
n	Refers to reaction orders
1, 2	Refer to reactions

Exercises

1. Study the system for the kinetic case $n_{A1} = n_{A2}$ and $n_{B1} < n_{B2}$. Run the reactor (i) semi-continuously with slow feeding of B and (ii) as a batch reactor with B charged initially to the reactor and zero feed of B. Compare the results obtained for the two differing modes of reactor operation.
2. Repeat Exercise 1 but for the kinetic case $n_{B1} > n_{B2}$.

3. Study the semi-continuous mode of operation further, using different values of feed rate and feed concentration to the reactor. Determine the feeding conditions that are most beneficial in terms of selectivity.
4. Assign arbitrary cost values ($/kmol) for the reactants A and B, a profit value for the product P and waste disposal and handling charges for the waste Q. Modify the program to incorporate these cost values and define a net cost function for the reaction and hence determine the best "environmental" operating condition. Study the effect of differing cost values on the above optimum.

Results

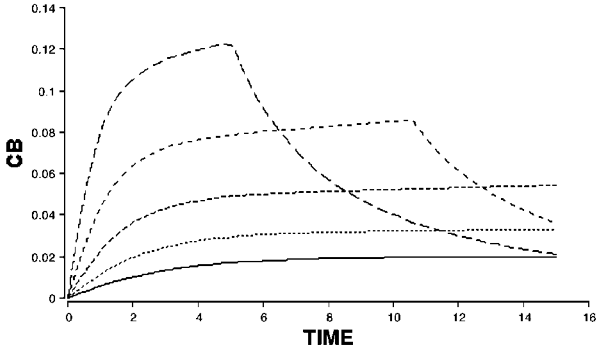


Fig. 2 Concentration of B for five feeding rates from F=0.005 to 0.1 m^3/min.

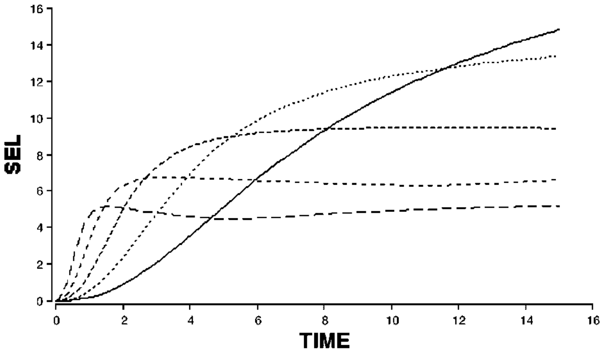


Fig. 3 Selectivity for P for the five feeding rates of Fig. 2.

5.5.2
SEMISEQ – Sequential-Parallel Reactions in a Semi-Continuous Reactor

System

A complex reaction is run in a semi-batch reactor with the purpose of improving the selectivity for the desired product P, compared to that of the waste Q, which is costly to treat and dispose. The kinetics are sequential with respect to components A, P and Q but are parallel with respect to B. The relative magnitudes of the orders of the two reactions determine the optimal feeding policy.

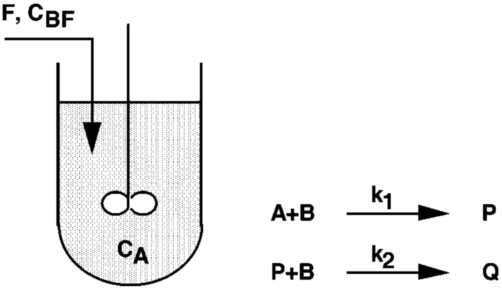


Fig. 1 Complex sequential reactions in a semi-continuous reactor.

Model

The total material balance under constant density conditions is

$$\frac{dV}{dt} = F_B$$

and the component balances are

$$\frac{d(VC_A)}{dt} = -r_1 V$$

$$\frac{d(VC_B)}{dt} = F\,C_{BF} - r_1 V - r_2 V$$

$$\frac{d(VC_P)}{dt} = r_1 V - r_2 V$$

$$\frac{d(VC_Q)}{dt} = r_2 V$$

The kinetic model equations are

$$r_1 = k_1 C_A^{n_A} C_B^{n_{B1}}$$

$$r_2 = k_2 C_P^{n_P} C_B^{n_{B2}}$$

The relative magnitudes of the orders of reaction, n_{B1} and n_{B2}, determine whether the concentration C_B in the reactor should be maintained high or low. The total reaction time must be adjusted such that product P is obtained at its maximum concentration, and this will also influence how B should be fed to the reactor.

Program

If the feeding rate is high the maximum reactor volume may be reached, which will cause the feeding rate of B to stop. The reaction then continues batchwise until the simulation is stopped. In the program the reaction orders are set as $n_A = n_P = 1$ and $n_{B1} < n_{B2}$. The selectivity for the desired product will be highest at the lowest feeding rates, since the desired reaction is then promoted by low concentrations of B.

The objective function used here, OBJ, assumes that product concentration, CP, product purity, Pfrac, and productivity, PROD, are important factors.

Nomenclature

Symbols

C	Concentration	kmol/m^3
V	Volume	m^3
F	Flow rate	m^3/min
r	Reaction rate	kmol/m^3 min

Indices

A, B, P, Q	Refer to components
F	Refers to inlet feed
n	Refers to reaction orders
1, 2	Refer to reactions

Exercises

1. Determine the optimal time to stop the reaction for a range of input flow rates to the reactor, such that the amount of product is greatest. How do the values of k_1 and k_2 influence this?
2. Study the influence of flow rate from the standpoint of maximum production of desired product P and for the minimisation of waste Q. Discuss the meaning and significance of the function OBJ. Study the influence of flowrate on its maximum value. How do the selectivity SEL and the maximum product concentration CP change with flowrate?
3. Study the system for the kinetic case $n_A=n_P=1$ and $n_{B1}<n_{B2}$. Run the reactor (i) semi-continuously with slow feeding of B and (ii) as a batch reactor with B charged initially to the reactor and zero feed of B. Compare the results obtained for the two differing modes of reactor operation.
4. Plot the ratio of the reaction rates for a range of conditions as an aid in understanding the effects of Exercise 2.
5. Modify the objective function to simulate a larger importance of investment costs by introducing an exponent for PROD larger than 1. How does the value of the exponent influence the value of the objective function OBJ? How is the time of the maximum of the objective function changed?
6. Assign the following cost values (\$/kmol) for the reactants A (300) and B (100), a profit value for the product P (500) and waste disposal and handling charges for the waste Q (50). Modify the program to incorporate these cost values, define a net cost function for the reaction only considering these raw material and waste treatment costs and determine the best operating conditions. How strongly does the cost of A influence the total economics. How much does a 10% difference make?

Results

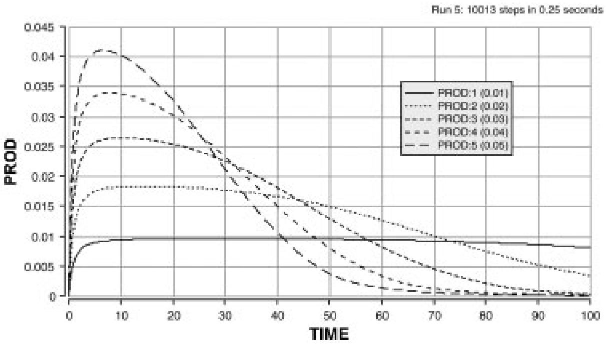


Fig. 2 Multiple runs showing the productivity PROD as a function of time for five feed rates of B between 0.05 and 0.01 m^3/min. The highest feed rate gives the lowest selectivity.

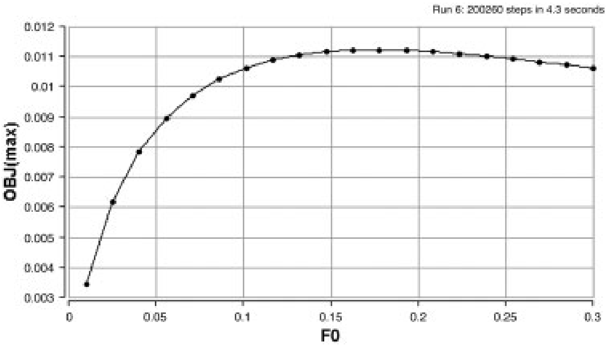


Fig. 3 Parametric run plotting the maximum in the objective function as a function of feed rate of B 0.01 to 0.3 m^3/min.

5.5.3
HMT – Semi-Batch Manufacture of Hexamethylenetetramine

System

Aqueous ammonia is added continuously to an initial batch charge of formaldehyde solution. The reaction proceeds instantaneously and is highly exothermic.

$$4\,NH_3 + 6\,HCHO \rightarrow N_4(CH_2)_6 + 6\,H_2O$$

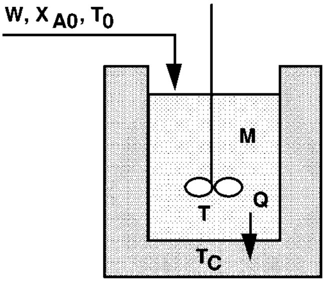


Fig. 1 Variables for the HMT example.

Model

For the semi-batch operation the total mass balance is

$$\frac{dM}{dt} = W$$

For the instantaneous reaction, the rate is equal to the reactant feed rate. The energy balance then becomes

$$M\,c_p\frac{dT}{dt} = W\,c_p(T_0 - T) + W\,X_{A0}(-\Delta H) - UA(T - T_c)$$

where X_{A0} is the mass fraction of ammonia in the feed stream.

Program

Since the reaction rate is instantaneous, this is set equal to the feed rate of ammonia.

Nomenclature

Symbols

A	Heat exchange area	m^2
c_p	Specific heat	kJ/kg C
M	Mass in reactor	kg
T and Temp	Temperature	C
U	Overall heat transfer coefficient	kJ/m^2 C
W	Mass feeding rate	kg/h
X_{A0}	Ammonia feed mass fraction	kg/kg
X_{F0}	Formaldehyde charge fraction	kg/kg
ΔH	Heat of reaction	kJ/kg

Indices

c	Refers to cooling
F	Refers to formaldehyde
0	Refers to feed values

Exercises

1. Find the size of cooling area required such that the reactor temperature just rises to 100 °C, by the end of the feeding at 90 min time.
2. Carry out simulations with differing inlet temperatures, initial charges and feeding rates.

Results

The results indicate that the mass flow rate has a strong influence on the reactor temperature.

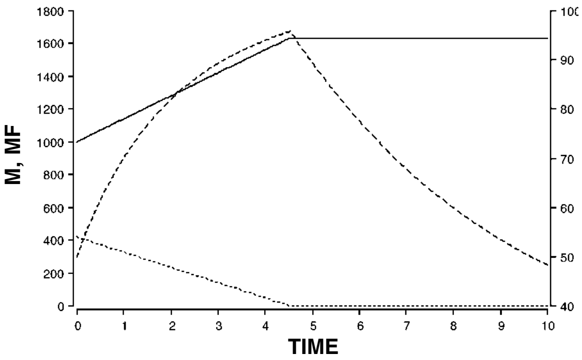


Fig. 2 Time profiles for total mass M, mass of formaldehyde MF and temperature. A slider for cooling area A was used to find the value necessary to keep T<100 °C.

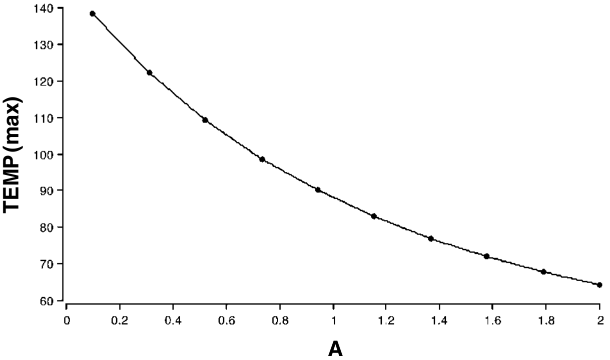


Fig. 3 Parametric run giving the maximum temperature as a function of A.

Reference

Smith, J. M. (1970) Chemical Engineering Kinetics, 2nd edition, McGraw-Hill.

5.5.4
RUN – Relief of a Runaway Polymerisation Reaction

System

The manufacture of a polyol lubricant by the condensation of an alcohol with propylene oxide in a semi-batch reactor proceeds according to the following reaction

$$C_4H_9OH + (n+1)C_3H_6O \rightarrow C_4H_9(OC_3H_6)_nOCH_2CHOHCH_3 + \text{heat}$$

The reaction is highly exothermic and the reactor contains large quantities of volatile oxide. Careful control of temperature is therefore required to avoid a runaway reaction and excessive pressure generation.

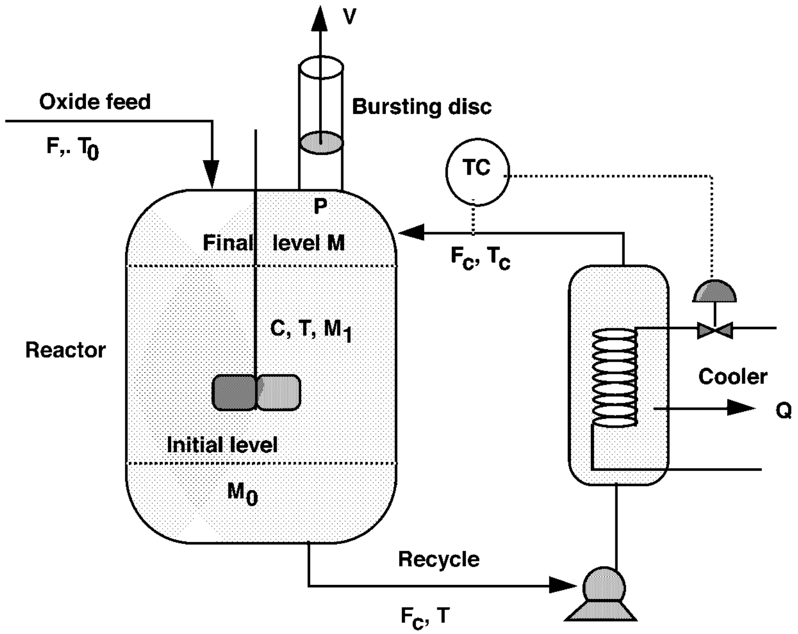


Fig. 1 Polymerisation reactor with its cooling unit and bursting disc.

The alcohol is charged initially to the reactor and the oxide is then fed to the reactor at constant rate. Heat generated by reaction is removed via an external heat transfer loop. In this, the batch contents are recycled through an external cooler with sufficient capacity to maintain a constant return temperature to the reactor. With high rates of cooling the reactor operation is stable, but a product of low molecular weight is produced. As the cooling is decreased, higher molecular weight product is obtained, but at the risk of a runaway reaction and reactor failure. In the event of this or the case of a cooling failure, a bursting disc in the reactor will rupture and the feed of oxide would usually be stopped. This will discharge oxide vapour to the atmosphere.

The simulation emphasises that when reactions start to run away, they do so extremely fast. In this example the rate of pressure generation is compounded by the double exponential terms in the Arrhenius and vapour pressure equations.

Model

The total mass balance is

$$\frac{dM}{dt} = F - V$$

where M is the reactor mass at time t (kg) and V is the vapour venting rate (kg/min) and F is the feed rate (kg/min).

The oxide component mass balance is

$$\frac{d(MC)}{dt} = F - V - R_1$$

where C is the oxide concentration (kg/kg) and R_1 is the oxide reaction rate (kg/min).

The mass of oxide reacted is given by

$$\frac{dX}{dt} = +R_1$$

where X is the mass of oxide reacted at time t.

The energy balance is

$$Mc_p \frac{dT_R}{dt} = Fc_p(T_0 - T_R) - V\lambda - R_1(-\Delta H) - Q$$

where T_R is the temperature of reaction (°C), Q is the rate of cooling (kJ/min) and λ is the heat of vaporisation of the oxide.

The heat removed via the recirculation through the external cooler is given by

$$Q = F_c c_p(T_R - T_c)$$

where F_c is the recycle mass flow rate (kg/min).

The reaction kinetics are given by

$$R_1 = k\,MC \text{ (kg oxide/min)}$$

where

$$k = Ze^{-\frac{E}{R(T_R+273)}}$$

The polymer molecular weight is

$$\mathrm{MW} = \frac{\mathrm{M_0 + X}}{\mathrm{N}}$$

where N is the kmol of initial alcohol charge.

Assuming instantaneous equilibrium, the reactor pressure and oxide vapour pressure is given by:

$$\mathrm{P} = \left[e^{\left(\frac{3430}{\mathrm{T_R}+273}+11.7\right)} + 1.45 \times 10^3\ \mathrm{MW} \right] \mathrm{C}$$

The vapour discharge rate is given by the following.

(1) For normal conditions and up to disc rupture

$$\mathrm{V} = 0$$

(2) For sonic discharge to atmospheric pressure

$$\mathrm{V} = \frac{\mathrm{k_v\, 0.85\, P}}{\sqrt{\mathrm{T_R} + 273}}\ \text{kg/min for P} > 1.9\ \text{bar}$$

(3) For subsonic discharge for $1 < P < 1.9$ bar

$$\mathrm{V} = \frac{\mathrm{k_v\, P}}{\sqrt{\mathrm{T_R} + 273}} \sqrt{1 + (1/\mathrm{P})^2}\ \text{kg/min}$$

where k_v is the valve discharge coefficient.

Program

The MADONNA program RUN with KV = 0 represents operation of the reactor under zero venting (V = 0) conditions, i.e., the bursting disc remains closed. With KV > 0 (100–1000) the program simulates the performance under emergency venting conditions. The program will continue to run unless coolant failure occurs, corresponding to FC = 0.

The program ensures that the bursting disc remains integral up to the bursting pressure, that the vapour discharge is sonic for reactor pressures greater than critical, that the discharge is subsonic for pressures less than critical and that the discharge stops when the pressure is atmospheric. The feed rate is programmed to either stop or continue following disc failure.

For convenience, the exit temperature from the cooler, T_c, is assumed equal to the feed temperature, T_0, i.e., the heat transfer capacity of the cooler is in large excess.

This program contains an example of conditional statements. A conditional variable DISK is defined such that if DISK = 1 then the bursting disk is intact, and if DISK = 0 the disk has burst. The discharge velocity through the disk varies with pressure as given by the complex conditional statement in the partial listing below:

```
{Example RUN}

{Vapor pressure in reactor}
P=(EXP(-3430/(TR+273)+11.7)+1.45E-3*MW)*C
Limit P>=1

{Bursting disc control: If Disk=1 then bursting disk OK; if
Disk=0 disk has burst}
F=IF (Disk<1) THEN 0 ELSE F0 {Feed flow rate of oxide, kg/min.
Oxide feed shuts off on bursting. This can be deactivated to
maintain feeding}

{Venting velocity control}
V=IF(Disk<1 AND P>1.9) {Velocity through disk varies
                        with P}
   THEN 0.85*KV*P/SQRT(TR+273)
     ELSE IF (Disk<1 AND P<=1.9 AND P>1.1)
       THEN KV*P/SQRT(TR+273)*SQRT(1+(1/P)*(1/P))
         ELSE IF P<=1.1
           THEN 0.0
             ELSE 0

MW=(M0+X)/N   {Molecular weight of polymer at any time,
               kg/kmol}
R1=K*MC   {Rate of polymerization reaction, kg oxide/min}
K=Z*EXP(-E/(R*(TR+273))) {Arrhenius relation}

{Total mass balance taking into account the initial alcohol M0
and the oxide fed and vaporized}
d/dt(M)=F-V      {Total mass balance}
d/dt(MC)=F-V-R   {Component mass balance for oxide}
LIMIT MC>=0      {Prevents negative values}
C=MC/M           {Mass fraction conc, kg/kg}
LIMIT C>=0       {Prevents negative values}

{Heat balance, considering flow, vaporization, reaction and
cooling}
d/dt(MTR)=(F*Cp*(T0-TR)-V*LAMBDA-R1*HR-FC*Cp*(TR-T0))/Cp
LIMIT MTR>=0
TR=MTR/M         {Calculation of TR}

d/dt(X)= R1      {Oxide reacted}
```

```
{State of the disk, starts at 1 and decreases quickly after
bursting; the value of Disk is used to detect if the disk has
burst. After bursting Disk=0}
d/dt(Disk)=-Fdisk
Limit Disk>=0
INIT Disk=1
Fdisk=IF(P>=PBURST) THEN 10 ELSE 0.0

{Cooling failure}
FC=IF TIME>=TIMEfail THEN 0.0 ELSE FC1   {Conditional re-
                                          cycle cooling flow}
TIMEfail=1500  {This is the time of failure, min}
```

Nomenclature

Symbols

C	Oxide concentration	kg/kg
c_p	Specific heat	kJ/kg C
E	Activation energy	kJ/mol
F	Oxide mass feed rate	kg/min
FC and FC1	Coolant flow rate	kg/min
λ	Heat of vaporisation of oxide	kJ/kg
M	Charge mass of alcohol	kg
MC	Mass of oxide	kg
MW	Molecular weight	kg/mol
Mol	Molecular weight of charge	kg/kmol
N	Initial alcohol charge	kmol
P	Reactor pressure	bar
P1	Bursting disc relief pressure	bar
P2	Maximum safe working pressure	bar
R	Gas constant	kJ/mol C
R1	Reaction rate	kg/min
T_R	Reaction temperature	C
t	Batch time	min
T_0	Charge, feed and recycle temperature	C
V	Venting rate	kg/min
X	Mass of oxide	kg
Z	Frequency factor	1/min
ΔH	Heat of reaction	kJ/kg

Indices

0	Refers to initial and inlet values
c	Refers to cooler

Exercises

1. Study the MADONNA program so that the conditional logic based on the IF_THEN_ELSE statements is fully understood.
2. With the bursting disc remaining closed (KV = 0 and V = 0), establish the minimum external recycle cooling flow (F_{c1}) needed to ensure stable operating conditions and satisfactory polymer product (Mol. wt = 2500). Determine the minimum cooling capacity required of the cooler. Study the effects of "runaway" following coolant failure by interactive computation. By carefully decreasing F_c from an initially "safe" value, the absolute limit of safe operation can be established. In this the reaction starts to run away, but then the reaction corrects itself by having consumed all the oxide and then continues with further stable operation.
3. Using the value of F_c found in Exercise 2, study the effect of differing valve discharge capacities (K_V) following cooling failure at different stages of reaction time ($F_c = 0$).
4. Run the simulation under disc-bursting conditions for both with and without shutting off the feed.
5. As an alternative to venting the vapour to atmosphere, the vapour may be condensed and returned to the reactor. Modify the program accordingly and study the resultant behaviour. See simulation examples REFRIDGE1 and REFRIDGE2.
6. Alter the program to include a complete model for the heat exchanger. This will allow a more realistic calculation of the heat removed.

Result

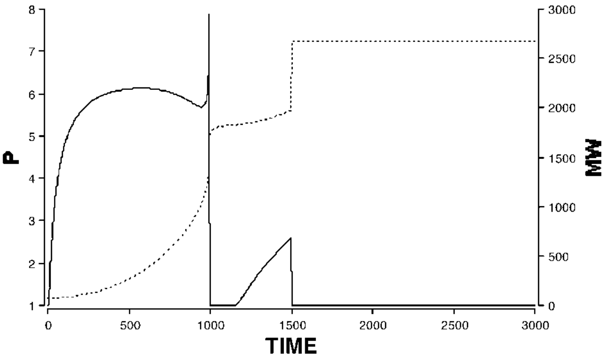


Fig. 2 Set at the point of stable operation the pressure increases until the oxide MC is consumed (Fig. 3) and then at lower temperature the process continues.

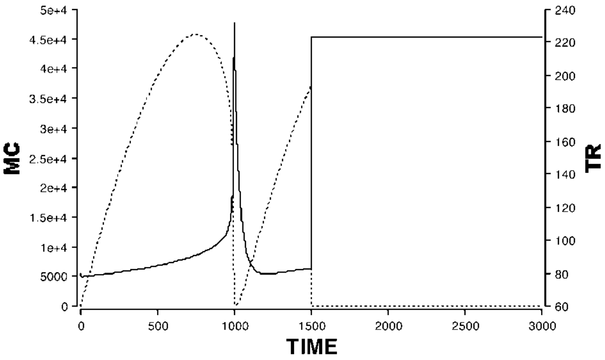


Fig. 3 The run of Fig. 2, showing the oxide MC falling to zero and the process continuing at lower temperature.

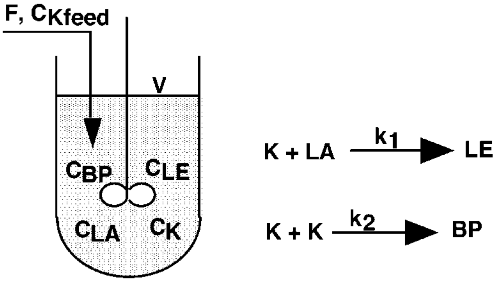
References

Kneale, M. and Forster, G.M. (1968) I. Chem. E. Symp. Series No. 25, 98.
Kneale, M. and Binns, J.S. (1977) I. Chem. E. Symp. Series No. 49.

5.5.5
SELCONT – Optimized Selectivity in a Semi-Continuous Reactor

System

Keller (1998) describes the semi-continuous reaction process of a vinyl ketone K with lithium acetylide LA to yield lithium ethinolate LE an intermediate in the vitamin production. In an undesired side reaction an oligomer byproduct BP is produced. During the process, reactant K is fed to the semi-batch reactor at a rate to maximize the selectivity for LE.



$$K + LA \xrightarrow{k_1} LE$$

$$K + K \xrightarrow{k_2} BP$$

Fig. 1 Semi-continuous reactor with feeding of ketone reactant.

Model

The total balance for the semi-batch reactor assuming constant density is

$$\frac{dV}{dt} = F$$

Written in terms of masses (C_iV) the component balances are

$$\frac{d(C_{LA}V)}{dt} = r_1V$$

$$\frac{d(C_{LE}V)}{dt} = -r_1V$$

$$\frac{d(C_KV)}{dt} = F\,C_{Kfeed} + r_1V + r_2V$$

$$\frac{d(C_{BP}V)}{dt} = -r_2V$$

and the concentrations for each component i are found from relations of the form $C_i = C_iV/V$.

The reaction rates are known to be given by

$$r_1 = -k_1C_KC_{LA}$$

$$r_2 = -k_2C_K^2$$

An objective function can be defined with respect to the positive impact by the productivity of LE and the negative contribution by that of BP weighted by a factor α.

$$OF = \frac{C_{LE}V - C_{BP}V\alpha}{t_B}$$

The final time t_B is reached when the reactor is full and when the residual concentration of K is 0.01.

Exercises

1. Find the optimal constant feeding rate of ketone to the reactor for $\alpha = 50$.
2. Investigate the influence of the value of α on the optimum.
3. Try to find a higher value for the objective function by using two time periods with two different constant feeding rates. Find the optimal values for the time periods and the flow rates.

4. Assume a ramp function for the flow rate ($F = F_0 + kt$) and find the values of F_0 and k which give the highest value for the objective function. Remember that F must remain positive.
5. Try to improve the value of the objective function by using a PI-controller to maintain constant selectivity throughout the batch, where

$$\mathrm{SEL} = \frac{r_1}{r_2 + r_1}$$

Find the value of the selectivity setpoint which gives the highest value of the objective function, as defined above with $a = 50$. Compare the feeding profile found with those found in the previous exercises.

Nomenclature

C	Concentration	$\mathrm{kmol/m^3}$
k	Rate constants	$\mathrm{m^3/kmol\ h}$
F	Flow rate of feed	$\mathrm{m^3}$
OF	Objective function	kmol/h
r	Reaction rate	$\mathrm{kmol/m^3\ h}$
V	Volume of reactor	$\mathrm{m^3}$
a	Penalty constant	–
SEL	Selectivity	–
T_B	Total time of reaction	h

Subscripts

BP	Refers to by-products
K	Refers to vinylketone
LA	Refers to lithium acetylide
LE	Refers to lithium ethinolate
1	Refers to desired reaction
2	Refers to undesired reaction

Results

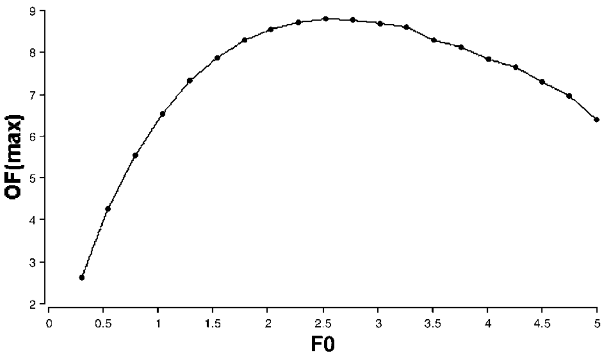


Fig. 2 The objective function varying with feed rate, with a maximum at 2.5 m^3/h.

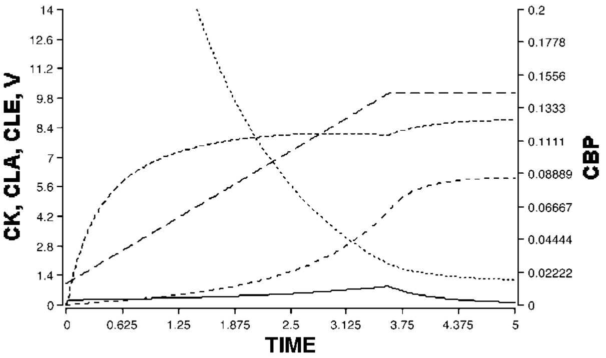


Fig. 3 Concentration profiles for a feed rate of 2.5 m^3/h. The feed is stopped at time=3.6 h.

Reference

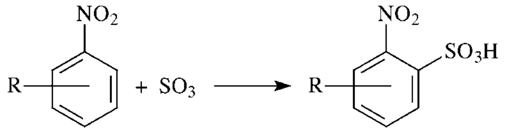
Keller, A. (1998) ETH PhD Dissertation No. 12607, Zürich

5.5.6

SULFONATION – Space-Time-Yield and Safety in a Semi-Continuous Reactor

System

In this case history, the control of the TMR_{ad} (adiabatic Time-to-Maximum-Rate) is to be achieved in a semi-continuous reactor process by the dynamic optimization of the feed rate. Here it is desired to have the highest possible space-time-yield STY and it is necessary to achieve a thermally safe process (Keller, 1998). The reaction involves the addition of a sulfur trioxide on a nitro-aromatic compound



The reaction takes place in the liquid phase of a semi-continuous process, which allows the feed rate manipulation to control the rate of heat release, as shown below.

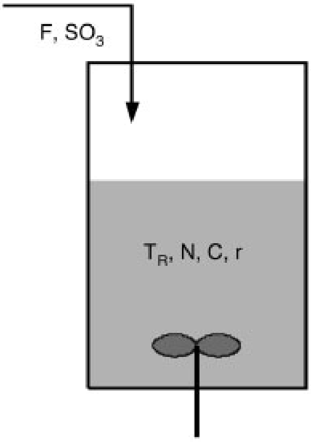


Fig. 1 Semi-continuous reactor process.

Model

Although the kinetics is not completely known, the following second order rate equation is assumed

$$r_1 = k_{1\infty} e^{\left(-\frac{E_{a1}}{RT_{RM}}\right)} [\text{Nitroaromatic}]\,[SO_3]$$

where T_{RM} is the temperature of the reacting mass, k_1 is the preexponentional factor and E_{a1} is the activation energy.

Decomposition reactions will occur at high temperatures and their rates are assumed to be first order as follows

$$r_2 = k_{2\infty} e^{\left(-\frac{E_{a2}}{RT_{RM}}\right)} [\text{Sulfonic acid}]$$

$$r_3 = k_{3\infty} e^{\left(-\frac{E_{a3}}{RT_{RM}}\right)} [\text{Nitroaromatic}]$$

The rate of heat production by the three reactions is written as

$$\frac{dQ_R}{dt} = -r_1(-\Delta H_{R1}) + r_2(-\Delta H_{R2}) + r_3(-\Delta H_{R3})$$

Calculating by dynamic mass balance the moles of trioxide at any time

$$\frac{dN_{SO_3}}{dt} = -r_1 V + F_D \frac{\Delta N_{SO_3}}{\Delta V}$$

where the experimental method of feeding allowed determining the concentration from the moles added for each volume. The initial volume of the reaction fluid is 3.7 m^3 having a total mass of 5586 kg. This consists of 18 kmol nitroaromatic compound dissolved in sulfuric acid. After the addition of 27.7 kmol SO_3 in the form of 65% oleum, the mass is increased by 4496 kg and the volume by 2.3 m^3. This determines $\Delta N_{SO_3}/\Delta V$.

Since the moles of trioxide will be less than the amount of nitroaromatic in the initial period of the process, trioxide will usually limit the extent of reaction. Later, the amount of trioxide will be larger. Therefore the maximum temperature that could be reached by complete conversion of the trioxide, MTSR, is

$$\mathrm{MTSR} = T_R + \frac{-\Delta H_{R1} N_{Acc}}{M\, c_{p,\,RM}}$$

N_{Acc} is the molar amount of the limiting reactant. From the MTSR the time to the maximum rate TMR_{ad} can be determined as

$$\mathrm{TMR}_{ad} = \frac{c_{p,\,RM}\, R\, \mathrm{MTSR}^2}{q_{ZR}\, E_{a2}}$$

Here q_{ZR} is the rate of heat produced by the decomposition reactions. The derivation of this equation is not shown here, but assumes a zero-order, worst-case reaction (Townsend and Tou, 1980).

The feed rate of SO_3 can be adjusted in three ways:

- Constant feed rate F_{p1} if CONTROLSET = 0 and STEPF = 0;
- Stepwise feed with feed rates F_1 to F_{20} with time interval PUMPTIME if CONTROLSET = 0 and STEPF > 0; or
- Controlled feeding depending on the calculated time-to-maximum rate TMR_{ad} if CONTROLSET > 0. The controller is of PI type and the set-point TMRset is slightly above the minimum tolerated time-to-maximum rate, TMR_{lim}, which is fixed at 24 hours. This is necessary because of possible slight undershooting of TMR_{ad} below TMR_{set}. In this case the flow rate is bound between 0 and F_{max}.

Objective Function

In this example only the main reaction and the two decomposition reactions are considered. For reasons of product quality, a conversion of 99% must be obtained. Also the production rate per unit volume, or space time yield, should be high. This can be expressed as

$$\mathrm{STY} = \frac{\mathrm{M_{prod}}}{\mathrm{V\, t_{Cycl}}}$$

For this reaction, that is first order for each of the reactants, it follows that the larger the concentrations the larger is the STY. However the safety of the process would be in jeopardy because $\mathrm{TMR_{ad}}$ also decreases with higher trioxide concentrations. For safety the lowest acceptable allowable value of $\mathrm{TMR_{ad}}$ is often taken as 24 h (Stoessel, 1993).

For calculation purposes an objective function is defined which penalizes the process if the value of $\mathrm{TMR_{ad}}$ takes a value lower than this value. It has the following form

$$\mathrm{J} = \frac{\mathrm{M_{prod}}}{\mathrm{V\, t_{Cycl}}} - \theta \int_0^{\infty} \Delta\mathrm{TMR_{ad}^2}\, \mathrm{dt}$$

such that

$$\Delta\mathrm{TMR_{ad}^2} = 0 \qquad \text{for} \qquad \Delta\mathrm{TMR_{ad}(lim)} - \Delta\mathrm{TMR_{ad}} \le 0$$

$$\Delta\mathrm{TMR_{ad}} = \mathrm{TMR_{ad}(lim)} - \mathrm{TMR_{ad}} \qquad \text{for} \qquad \Delta\mathrm{TMR_{ad}(lim)} - \Delta\mathrm{TMR_{ad}} \ge 0$$

Nomenclature

The definition of the symbols and their values are listed in the program.

Program

```
The program SULFONATION is on the CD. The line
Fp2 = IF CONTROLSET > 0 THEN Fpreg2 ELSE if STEPF > 0 THEN Fstep
ELSE Fp1
```

Serves to switch between the three selectable feed modes as described above.

The step feeding is programmed using nested if statements. 19 time points with a time interval of PUMPTIME (time1 to time time 19) are defined at which flow rate is switched to the next predefined value F2 to F20.

```
Fstep=
IF TIME<time1 THEN F1 ELSE
  IF TIME<time2 THEN F2 ELSE
    IF TIME<time3 THEN F3 ELSE
      IF TIME<time4 THEN F4 ELSE
        IF TIME<time5 THEN F5 ELSE
          IF TIME<time6 THEN F6 ELSE
            IF TIME<time7 THEN F7 ELSE
              IF TIME<time8 THEN F8 ELSE
                IF TIME<time9 THEN F9 ELSE
                  IF TIME<time10 THEN F10 ELSE
                    IF TIME<time11 THEN F11 ELSE
                      IF TIME<time12 THEN F12 ELSE
                        IF TIME<time13 THEN F13 ELSE
                          IF TIME<time14 THEN F14 ELSE
                            IF TIME<time15 THEN F15 ELSE
                              IF TIME<time16 THEN F16 ELSE
                                IF TIME<time17 THEN F17 ELSE
                                  IF TIME<time18 THEN F18 ELSE
                                    IF TIME<time19 THEN F19 ELSE
F20
```

In this way each individual flow rate can be freely adjusted or automatically optimized.

Exercises

1. Study the operation with constant feed rate. Set the variable CONTROLSET =0 for constant feeding. Here it is of interest to understand the operation by following the volume, flow rate, moles of A and B, accumulated moles of A and B, the amount of limiting reactant N_{acc}, concentrations of A, B and P, TMR_{ad}, STY and J. Check whether TMR_{lim} has been under-run.
2. Investigate the influence of temperature TR by running at slightly higher and lower temperatures. Watch changes in all variables listed in Exercise 1. See if safe conditions result, such that TMR_{ad} is always greater than 24 h.
3. Repeat the study of Exercise 2 for changes in feed rate.
4. Using the Parameter-Optimize feature in MADONNA, determine the maximum value of J in both programs (controlled and uncontrolled). Here the function to maximize is –J, since a minimum is sought.
5. Check to see that J was really a maximum using Parameter Plots. Plot also the STY values here.
6. Turn the controller on, repeat Exercise 1 and note the differences in results compared with the constant feed case of Exercise 1.

7. For the controlled case determine the optimal temperature using the Parameter-Optimize feature. How does this J value compare to that from Exercise 4?
8. Find out an optimal profile when using the step feeding alternative. After setting CONTROLSET=0 and STEPF=1 first try to find an optimal profile by manually adjusting F1 to F20. Make sure that TMR_{ad} is not dropping below TMR_{lim}.
9. Using the Parameter-Optimize feature in MADONNA, determine the maximum value of J by letting the program find the best values for F1 to F20. Define minimum flow rates 0. Compare now all three results using the overlay feature of MADONNA and adjusting CONTROLSET and STEPF.

References

Keller, A. H. (1998) „Stufengerechte Beurteilung und Optimierung der thermischen Prozesssicherheit mittels dynamischer Modellierung“. Diss. ETH #12607.

Stoessel, F. (1993) What is your thermal risk? Chem. Eng. Prog. October: 68–75.

Townsend, D. I. and Tou, J. C. (1989) Thermal hazard evaluation by an accelerating rate calorimeter. Thermochim Acta 37:1–30.

Results

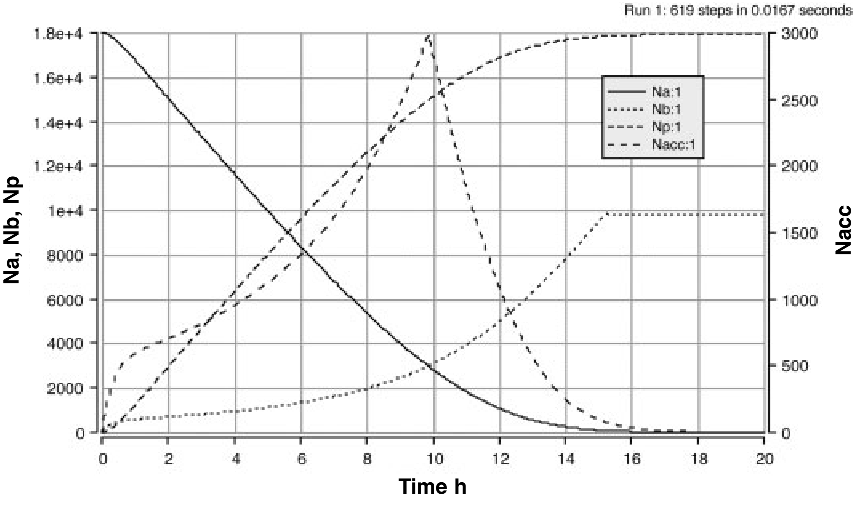


Fig. 1 Profiles of A, B, P and N_{acc} for constant feed rate.

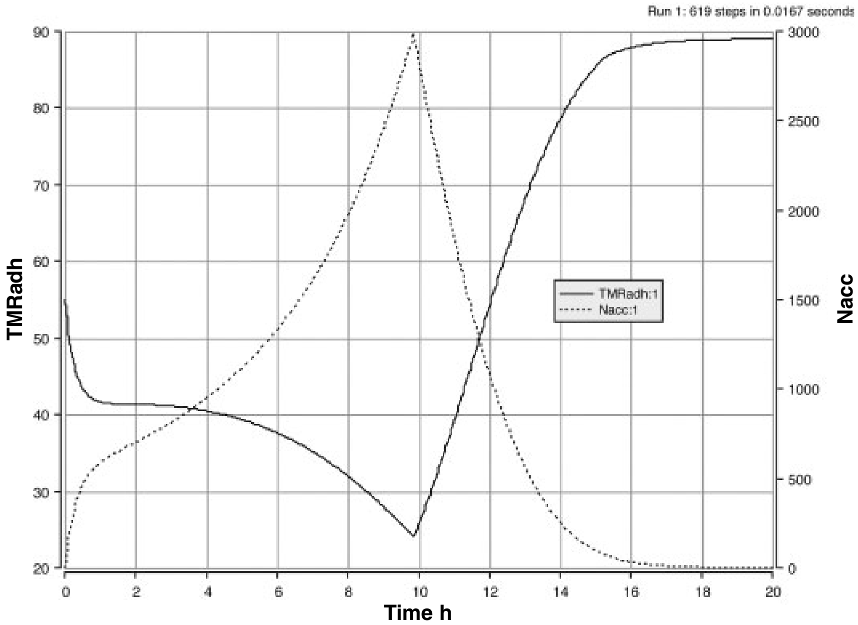


Fig. 2 Profiles of TMR_{ad} and N_{acc} for the run in Fig. 1.

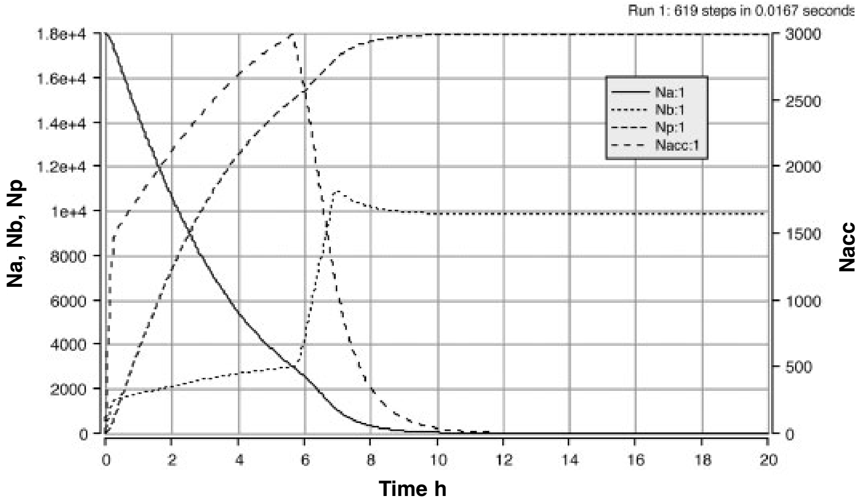


Fig. 3 Profiles of A, B, P and N_{acc} for controlled feed rate (controlset=1).

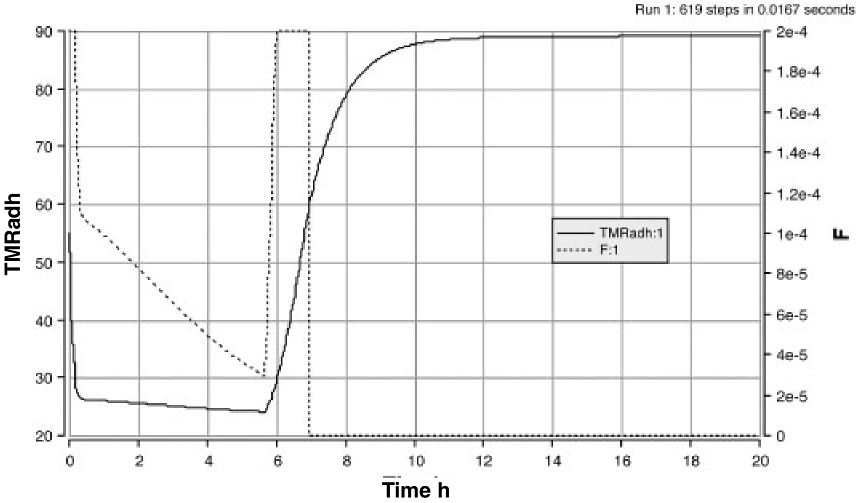


Fig. 4 Profiles of TMR_{adh} and F for controlled feed rate (stepfeed=1, $KP=1\times10^{-8}$).

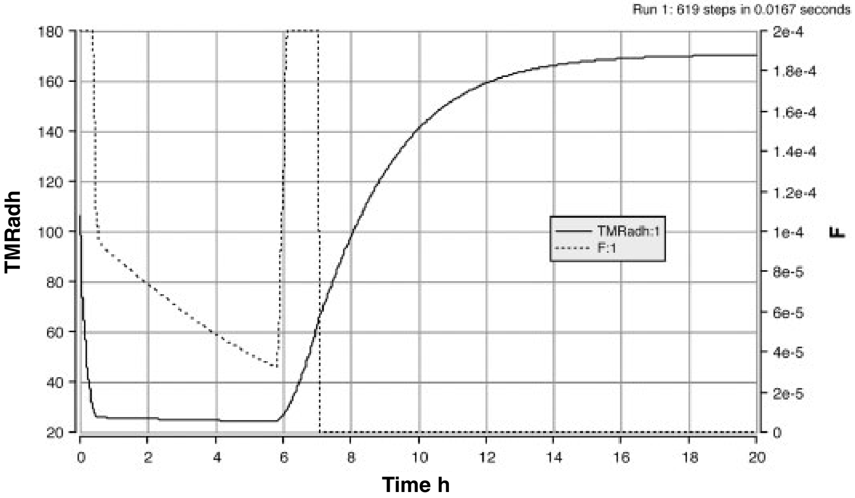


Fig. 5 Profiles of TMR_{adh} and F for controlled feed rate (controlset=1, $KP=1\times10^{-8}$) at lower temperature, 388 K.

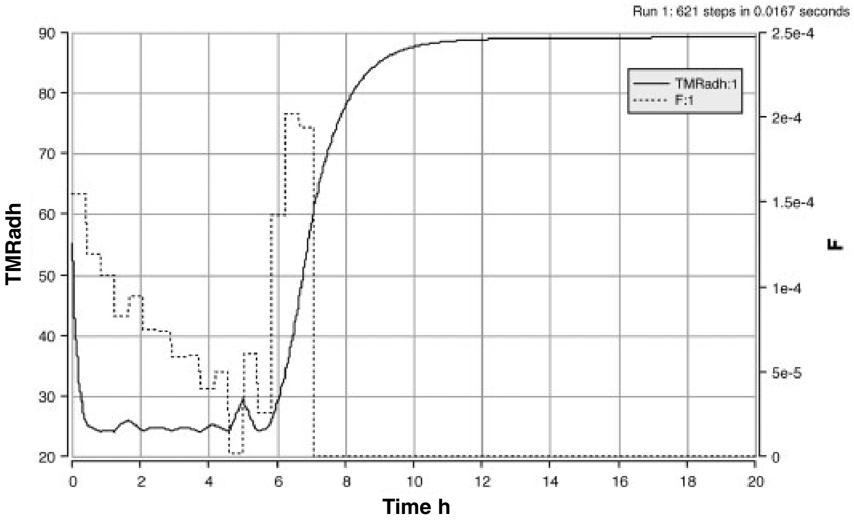


Fig. 6 Profiles of TMR_{adh} and F for a step feeding run.

5.6
Mixing-Model Examples

5.6.1
NOCSTR – Non-Ideal Stirred-Tank Reactor

System

In this model of non-ideal reactor mixing, a fraction, f_1, of the volumetric feed rate, F, completely bypasses the mixing in the reactor. In addition, a fraction, f_2, of the reactor volume, V, exists as dead space. F_3 is the volumetric rate of exchange between the perfectly mixed volume V_1 and the dead zone volume V_2 of the reactor.

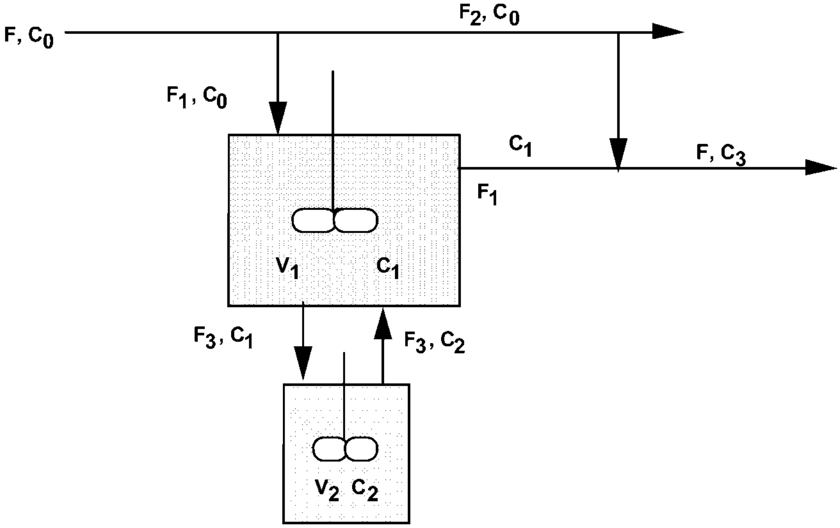


Fig. 1 The non-ideal flow reactor model.

Model

The reaction is assumed to be first order, where

$$r = kC$$

The component mass balances are as follows.

For the well-mixed volume

$$V_1 \frac{dC_1}{dt} = F_1(C_0 - C_1) + F_3(C_2 - C_1) - V_1 k_1 C_1$$

where $V_1 = (1 - f_2)V$ and $F_1 = (1 - f_1)F$.

For the dead space volume

$$V_2 \frac{dC_2}{dt} = F_3(C_1 - C_2) - V_2kC_2$$

where

$$V_2 = f_2V$$

and

$$F_3 = \alpha F$$

Note that the dead space is treated as having a region of uniform well-mixed composition.

For the reactor outlet

$$FC_3 = F_1C_1 + F_2C_0$$

where

$$F_2 = f_1F$$

For a perfectly mixed tank with outlet concentration C_4 and total volume V

$$V \frac{dC_4}{dt} = F(C_0 - C_4) - VkC_4$$

Program

Note that in the program that while the by-passing flow fraction f_1 (FRAC1) can be set to zero, the fractional dead space volume f_2 (FRAC2) cannot be set to zero without modifying the program. This would cause the derivative value for C_2 to be divided by a zero value for V_2.

Nomenclature

Symbols

C_0	Feed concentration	$kmol/m^3$
C_1	Active zone concentration	$kmol/m^3$
C_2	Deadzone concentration	$kmol/m^3$
C_3	Effluent concentration	$kmol/m^3$
C_4	Ideal tank concentration	$kmol/m^3$
F	Total flow rate	m^3/min
f_1	Fractional by-pass flow	–

F_2	By-pass flow rate	m^3/min
f_2	Dead volume fraction	–
F_3	Deadzone exchange flow	m^3/min
R	Rate constant	1/min
X	Fractional conversion	–
α	Fractional deadzone flow	–

Indices

0	Refers to feed
1	Refers to interchange flow and outlet concentration
2	Refers to dead volume region
3	Refers to deadzone flow

Exercises

1. Study the effects of fractional bypassing and fractional dead space volume on the steady-state conversion, X3, compared to that of the ideal tank, X4.
2. Note if K=0, the program generates a tracer step-response curve for the non-ideal reactor.
3. Study the effect of variations in the rate of exchange F3 between the two reactor volumes, by varying the value of ALPHA.
4. Modify the program to allow for zero dead space volume and study the effect of fractional bypassing only. Compare the results to that for a perfectly stirred tank.
5. Modify the system to that shown below by Froment and Bischoff (1990), in which the volumetric flow, F, having passed through a partial well-mixed volume, V_1, is then diverted such that a fraction, f, then passes through the residual volume, V_2, before rejoining the main flow stream. Formulate the model equations and record the F-curve response for the system for varying values of V_1 and V_2 keeping the total volume ($V=V_1+V_2$) constant and varying the values of f.

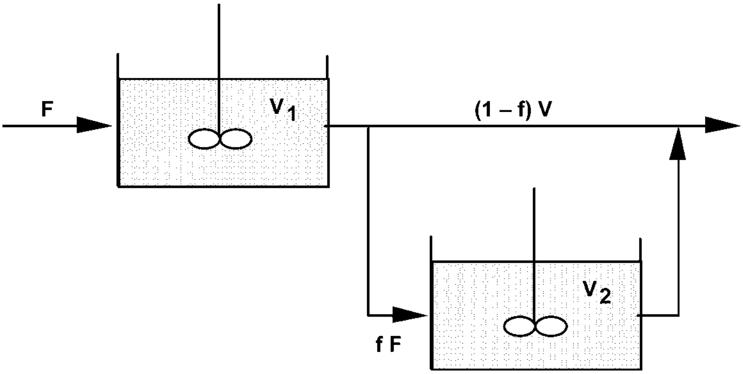


Fig. 2 Mixing model of Froment and Bischoff (1990).

Results

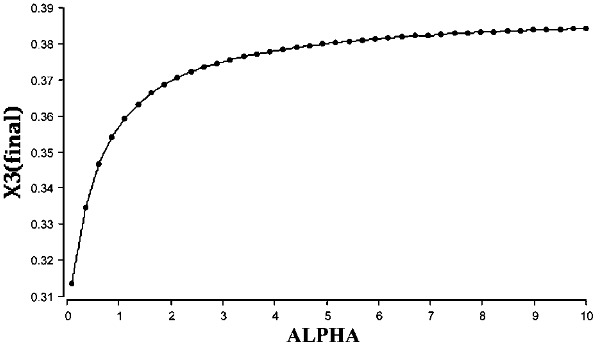


Fig. 3 A parametric run showing the influence of ALPHA from 0.1 to 10.

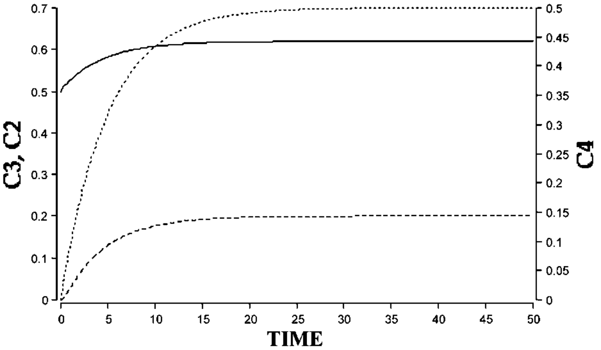


Fig. 4 A response of the reactor model to a step change in concentration. The well-mixed case C4 is shown for comparison.

Reference

Froment, G. F., Bischoff, K. B. (1990) Chemical Reactor Analysis and Design, 2nd ed., Wiley Interscience.

5.6.2
TUBEMIX – Non-Ideal Tube-Tank Mixing Model

System

Non-ideal mixing conditions in a reactor can often be modelled as combinations of tanks and tubes. Here a series of stirred tanks are used to simulate a tubular, by-passing condition.

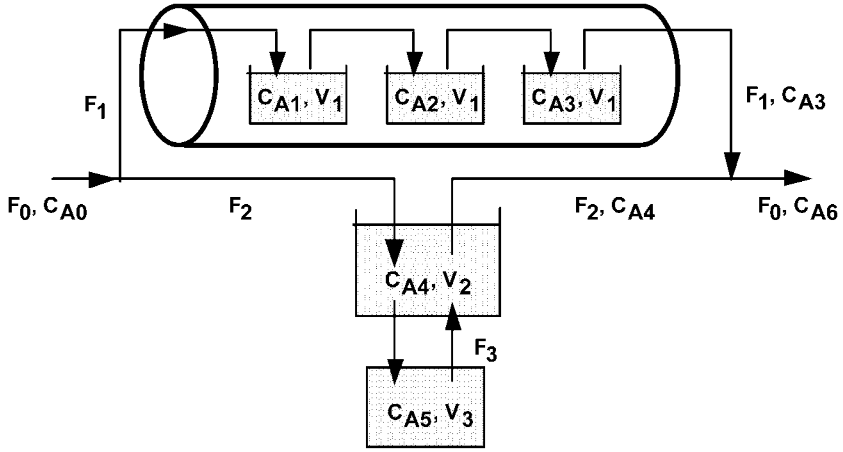


Fig. 1 A combined tank-tube mixing model.

Model

For the tubular by-pass flow representation, the balances for reactant A have the form

$$\frac{V_1 dC_{An}}{dt} = F_1(C_{An-1} - C_{An}) + r_{An}V$$

for each of the sections n = 1, 2, ... N.

The main tank reactor region has the balance

$$\frac{V_2 dC_{A4}}{dt} = F_2C_{A0} + F_3C_{A5} - F_2C_{A4} - F_3C_{A4} + r_{A4}V_2$$

The dead-zone region is balanced by

$$\frac{V_3 dC_{A5}}{dt} = F_3 C_{A4} - F_3 C_{A5} + r_{A5} V_3$$

The final outlet concentration is given by the balance at the mixing point

$$F_0 C_{A6} = F_1 C_{A3} + F_2 C_{A4}$$

The flow rates are given in terms of the flow fractions as

$$F_1 = F_0 R_1$$

and

$$F_3 = F_2 R_2$$

and the volumes are given by

$$V_2 = \frac{V_{tub}}{R_3}$$

and

$$V_3 = \frac{V_2}{R_4}$$

The reaction rates are

$$r_{An} = k\, C_{An}^{m}$$

where n refers to the section number and m refers to the reaction order.

Program

The program is written in array form so that the number of tanks within the tubular section can be varied.

Nomenclature

Symbols

C_{A0}	Feed concentration	kg/m^3
C_{Ainit}	Initial concentrations	kg/m^3
F_0	Feed to reactor system	m^3/min

F_1	Flow rate to tube	m^3/min
F_2	Flow rate to tank	m^3/min
F_3	Interchange flow rate	m^3/min
k	Reaction constant	various
m	Reaction order	
R_1	Feed fraction tube/tank	–
R_1	Flow fraction F_1/F_0	–
R_2	Feed fraction tank1/tank2	–
R_2	Flow fraction F_3/F_2	–
R_3	Volume fraction tube/tank1	–
R_4	Volume fraction tank1/tank2	–
V_1	Volume of tank sections in tube	m^3
V_2	Volume of main reactor section	m^3
V_3	Volume of deadzone section	m^3
V_{tub}	Volume of tube reactor	m^3

Results

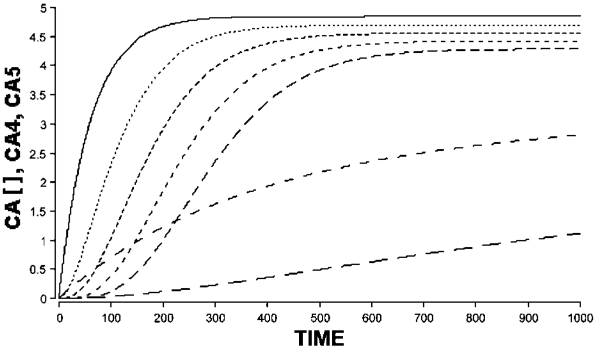


Fig. 2 Shown here for first-order reaction is a step response of the 5 tanks, as well as the slower responses of CA4 and CA5.

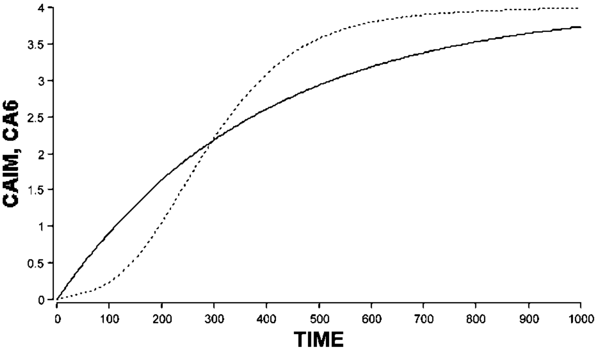


Fig. 3 From the run of Fig. 2, as an overall comparison, are shown the CA6 outlet response and the response for a completely mixed system, given by CAiM.

5.6.3
MIXFLO1 and MIXFLO2 – Mixed–Flow Residence Time Distribution Studies

System

The following systems represent differing combinations of ideal plug-flow, mixing, dead space, flow recycle and flow by-pass.

Case 1

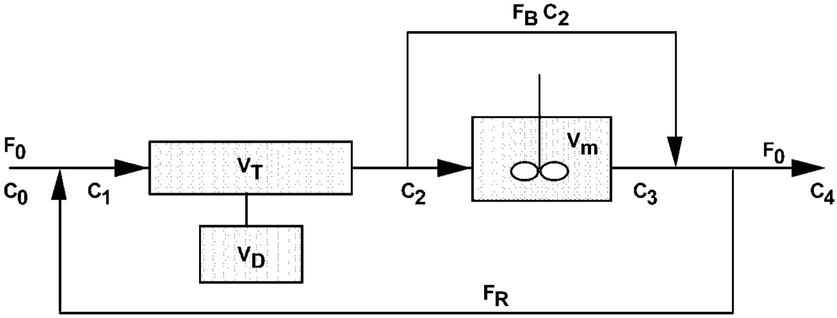


Fig. 1 Mixing model for residence time distribution Case 1.

Case 2

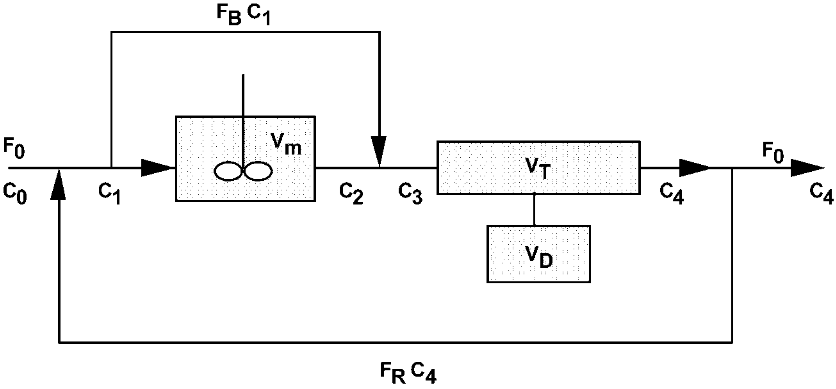


Fig. 2 Mixing model for residence time distribution Case 2.

It is desired to compare the residence time distributions (RTD) for these cases.

Model

Ideal plug-flow regions, such as V_T, are represented by standard Madonna time delay functions.

Case 1

The mixing junction is given by the steady-state balance,

$$F_0C_0 + F_RC_4 = (F_0 + F_R)C_1$$

Thus the concentration leaving the junction is

$$C_1 = \frac{F_0C_0 + F_RC_4}{F_0 + F_R}$$

For the plug-flow region V_T, the outlet concentration C_2 is equal to the input concentration C_1, but delayed in time by

$$\frac{V_T - V_D}{F_0 + F_R}$$

The well-mixed region is given by

$$V_m\frac{dC_3}{dt} = (F_0 + F_R - F_B)(C_2 - C_3)$$

The final outlet concentration is given by a steady-state junction relation as,

$$C_4 = \frac{F_BC_2 + (F_0 + F_RF_B)C_3}{F_0 + F_R}$$

Case 2

The relations used here are analogous to Case 1.

For the junction

$$C_1 = \frac{F_0C_0 + F_RC_4}{F_0 + F_R}$$

For the mixing tank

$$V_m\frac{dC_2}{dt} = (F_0 + F_R - F_B)(C_1 - C_2)$$

For the by-pass junction

$$C_3 = \frac{F_B C_1 + (F_0 + F_R F_B) C_2}{F_0 + F_R}$$

For the plug-flow time delay

$$C_4 \text{ is equal to } C_3 \text{ delayed in time by } \frac{V_T - V_D}{F_0 + F_R}$$

Program

The Madonna program MIXFLO1 models the situation of Case 1, and program MIXFLO2 models that of the Case 2. The plug-flow section of the plant is modelled with the time delay function, DELAYT. This is suitable for residence time distribution studies, but is not suitable to calculate the conversion for non-first order reactions. The Madonna logic is such that a dynamic concentration mixing point of finite volume is necessary within the program to provide an initial condition, owing to the time delay and the recycle stream.

Nomenclature

Symbols

V	Volume	m^3
F	Volumetric flow	m^3/s
C	Tracer concentration	kg/m^3

Indices

T	Refers to plug flow
M	Refers to mixing
D	Refers to dead space
B	Refers to by-pass
R	Refers to recycle
1, 2, 3, 4	Refer to positions according to figure

Exercises

1. Vary the relative system parameters VT, VD and VM for the two differing flow cases, keeping the total volume of the system constant. Compare the resulting residence time distributions.
2. Keeping the total volume of the system constant, vary the relative flowrates, F0, FB and FR and note the influence on the RTD's.

3. Evaluate the conversion for first-order reaction from a tracer pulse response curve using the method in example CSTRPULSE. Show that although the residence time distributions may be the same in the two cases, the overall chemical conversion is not, excepting for the case of first-order reaction.

Results

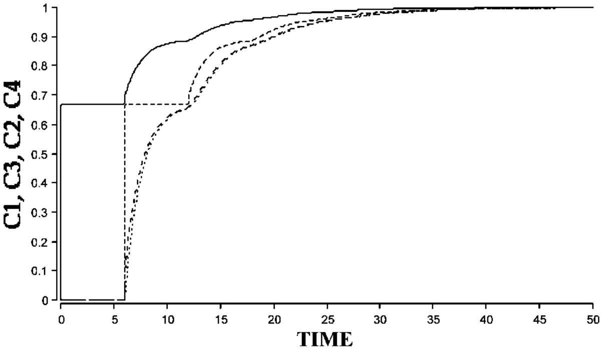


Fig. 3 For MIXFLO1 a step in C0 creates this response in C1, C2, C3 and C4. The time delay function gives a delay between C1 and C2.

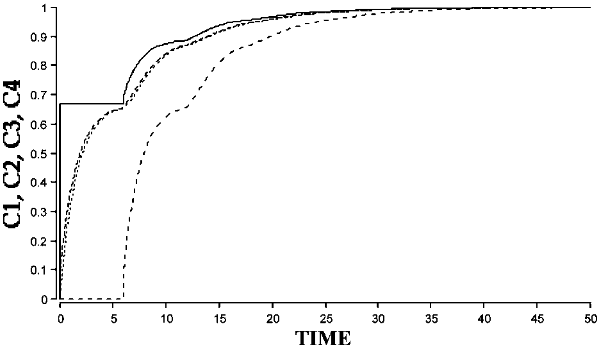


Fig. 4 For MIXFLO2 a step in C0 creates this response in C1, C2, C3 and C4. The time delay function gives a delay between C3 and C4.

Reference

Szekely, J., Themelis, N. J. (1971) Rate Phenomena in Process Metallurgy, Wiley Interscience.

5.6.4
GASLIQ1 and GASLIQ2 – Gas–Liquid Mixing and Mass Transfer in a Stirred Tank

System

The gas–liquid flow characteristics of stirred vessels depend both on the level of agitation and the rate of gas flow and can vary from the case of bubble column type operation to that of a full circulating tank, as shown in Fig. 1. The mixing characteristics and gas distribution obtained obviously exert a considerable influence on the rate of mass transfer obtained (Harnby et al., 1985).

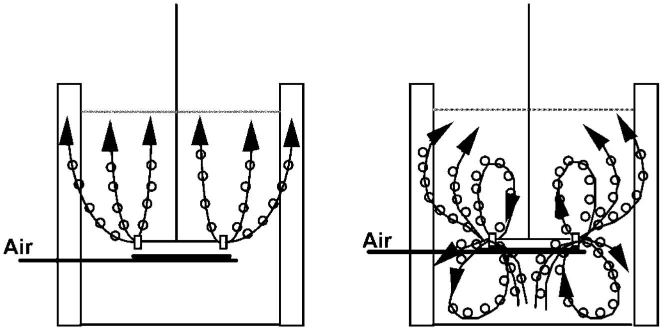


Fig. 1 Gas–liquid mixing modes: (a) bubble column behaviour (high gas flow, low rotor speed); (b) circulating tank behaviour (high rotor speed, reduced gas flow).

In this example it is required to model the behaviour of the mixing vessel according to the conceptual models indicated below.

Liquid Mixing

The basic liquid mixing pattern is assumed to remain constant, as shown in Fig. 2.

In this, the liquid acts as three well-stirred regions, the smaller one representing the region close to the impeller. The two larger ones represent the volumes of liquid above and below the impeller, with the flow from the impeller discharging equally into the two main tank regions.

Gas Mixing

The gas phase mixing is represented by three equally-sized tanks in series.

In the case of the full bubble column, the bottom gas phase mixed region is coincident with the impeller, and no significant gas mixing occurs below the impeller, in the lower region of the tank, as shown in Fig. 3. The dashed arrows in Figs. 3 and 4 represent mass transfer interchange between the gas space and liquid volumes of the tank. The liquid circulation, which is not shown, is identical to Fig. 2.

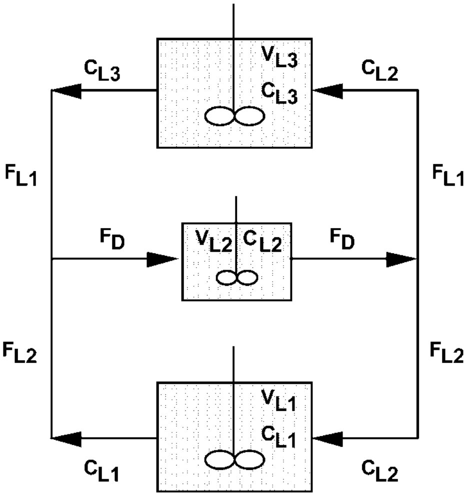


Fig. 2 Model for the liquid mixing pattern in a stirred tank.

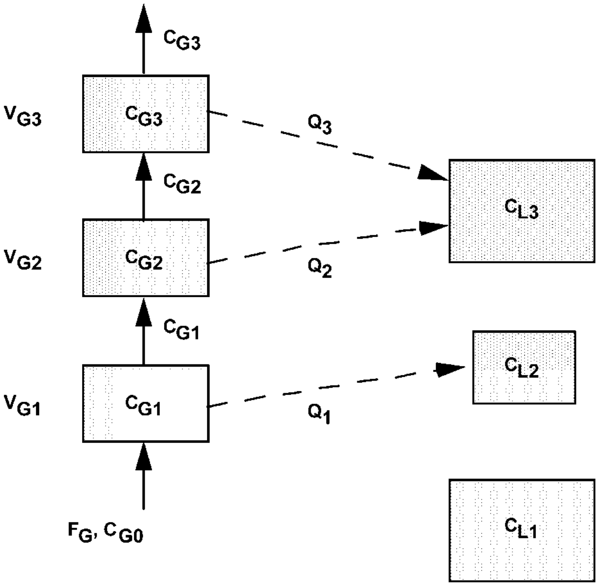


Fig. 3 Gas phase mixing pattern and mass transfer for full bubble column.

With full circulation, substantial gas phase mixing occurs in all tank regions, as shown in Fig. 4.

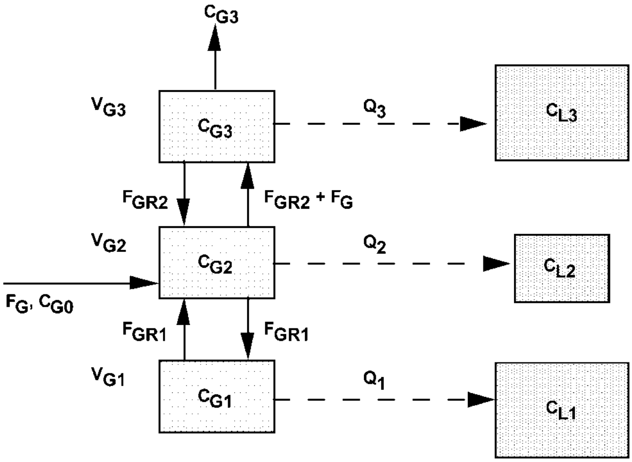


Fig. 4 Gas phase mixing and mass transfer for full circulation case.

Model

Bubble Column Operation

Liquid phase balances

$$V_{L1}\frac{dC_{L1}}{dt} = F_{L2}(C_{L2} - C_{L1})$$

$$\begin{aligned} V_{L2}\frac{dC_{L2}}{dt} &= F_{L2}C_{L1} + F_{L1}C_{L3} - F_D C_{L2} + Q_1 \\ &= F_{L2}(C_{L1} - C_{L2}) + F_{L1}(C_{L3} - C_{L2}) + Q_1 \end{aligned}$$

$$V_{L3}\frac{dC_{L3}}{dt} = F_{L1}(C_{L2} - C_{L3}) + Q_2 + Q_3$$

Pump discharge rate

$$F_D = F_{L1} + F_{L2}$$

Gas phase balances

$$V_{G1}\frac{dC_{G1}}{dt} = F_G(C_{G0} - C_{G1}) - Q_1$$

$$V_{G2}\frac{dC_{G2}}{dt} = F_G(C_{G1} - C_{G2}) - Q_2$$

$$V_{G3}\frac{dC_{G3}}{dt} = F_G(G_{G2} - C_{G3}) - Q_3$$

Rates of mass transfer

$$Q_1 = K_La(C^*_{L1} - C_{L2})V_{G1}$$

$$Q_2 = K_La(C^*_{L2} - C_{L3})V_{G2}$$

$$Q_3 = K_La(C^*_{L3} - C_{L3})V_{G3}$$

The equilibrium relationships are represented by means of Henry's law where

$$C^*_{L1} 0 \frac{RTC_{G1}}{H}$$

$$C^*_{L2} = \frac{RTC_{G2}}{H}$$

$$C^*_{L3} = \frac{RTC_{G3}}{H}$$

Full Circulation

Liquid phase balances

$$V_{L1}\frac{dC_{L1}}{dt} = F_{L2}(C_{L2} - C_{L1}) + Q_1$$

$$V_{L2}\frac{dC_{L2}}{dt} = F_{L2}(C_{L1} - C_{L2}) + F_{L1}(C_{L3} - C_{L2}) + Q_2$$

$$V_{L3}\frac{dC_{L3}}{dt} = F_{L1}(C_{L2} - C_{L1}) - Q_1$$

Gas phase balances

$$V_{G1}\frac{dC_{G1}}{dt} = F_{GR1}(C_{G2} - C_{G1}) - Q_1$$

$$V_{G2}\frac{dC_{G2}}{dt} = F_GC_{G0} + F_{GR1}(C_{G1} - C_{G2}) + F_{GR2}C_{G3} - (F_{GR2} + F_G)C_{G2} - Q_2$$

$$V_{G3}\frac{dC_{G3}}{dt} = (F_{GR2} + F_G)(C_{G2} - C_{G3}) - Q_3$$

Rates of mass transfer

$$Q_1 = K_La(C^*_{L1} - C_{L1})V_{G1}$$

$$Q_2 = K_La(C^*_{L2} - C_{L2})V_{G2}$$

$$Q_3 = K_La(C^*_{L3} - C_{L3})V_{G3}$$

The equilibrium relationships are represented by Henry's law as before.

Program

Program GASLIQ1 simulates the case of the full bubble column and program GASLIQ2 that of the full circulation case. For simplicity a constant value of overall mass transfer capacity coefficient, K_La, is assumed to apply for all the liquid regions, but the value obtained in the case of full circulation is taken as five times that for the bubble column.

Nomenclature

Symbols

V	Volume	m^3
F	Volumetric flow rate	m^3/s
C	Oxygen concentration	$kmol/m^3$
Q	Rates of oxygen transfer	kmol/s
K_La	Mass transfer capacity coefficient	1/s
R	Ideal gas constant	$m^3atm/kmol\ K$
T	Temperature	K
H	Henry's law constant	$m^3atm/kmol$

Indices

0, 1, 2, 3	Refer to streams and zones (see figures)
L	Refers to liquid
G	Refers to gas
R	Refers to recycle
*	Refers to equilibrium

Exercises

1. Simulated tracer experiments can be performed on either program by setting $K_La=0$ and starting with suitable initial conditions and inlet concentrations. The methods given in example CSTRPULSE can be used for this.
   For example:
   a) In GASLIQ1 set initial values as follows: CL2 = 1, CL1 and CL3 = 0. Observe the tracer response curve for different values of FL1 and FL2.
   b) In GASLIQ2 set CGI = 0 and the inflow CG0 = 1. Observe the response of the outflow CG3 for various values of the circulation flow FGR1 and FGR2.
2. Set K_La to a suitable value and experiment with the influence of the mixing parameters FL1 and FL2 in GASLIQ1 and FGR1 and FGR2 in GASLIQ2.

Results

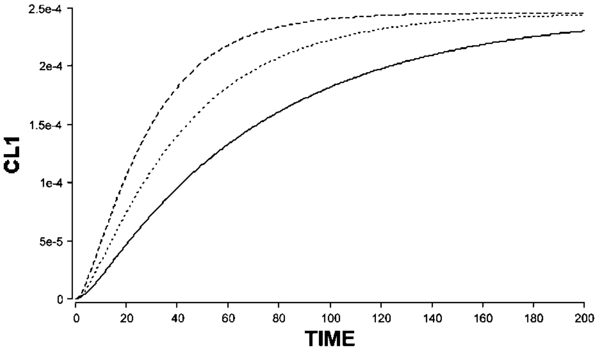


Fig. 5 GASLIQ1 with transfer showing the response of CL1 for three values of FL1 = FL2 from 0.005 to 0.02 m^3/s.

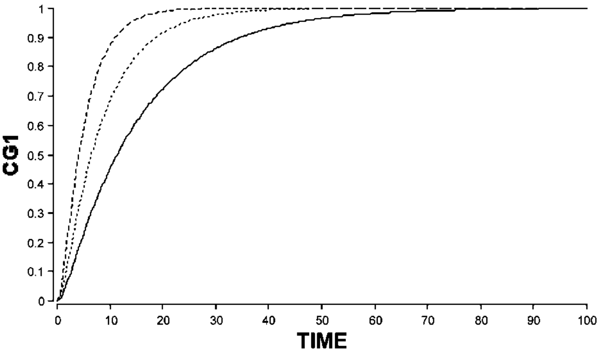


Fig. 6 Step tracer response of GASLIQ2 without transfer showing the response of CG1 for three values of FGR1 = FGR2 from 0.0005 to 0.002 m^3/s.

Reference

Harnby, N., Edwards, M. F. and Nienow, A. W. (Eds.) (1985) Mixing in the Process Industries, Butterworths.

5.6.5
SPBEDRTD – Spouted Bed Reactor Mixing Model

System

In this example, a stirred-tank model is employed to model the mixing behavior of an air–solid, spouted, fluidised-bed reactor. The central spout is modelled as two tanks in series, the top fountain as a further tank and the down flowing annular region of the bed as six equal-sized tanks in series. It is assumed that a constant fraction of the total solids returns from each stage of the annular region into the central two-tank region, as depicted below.

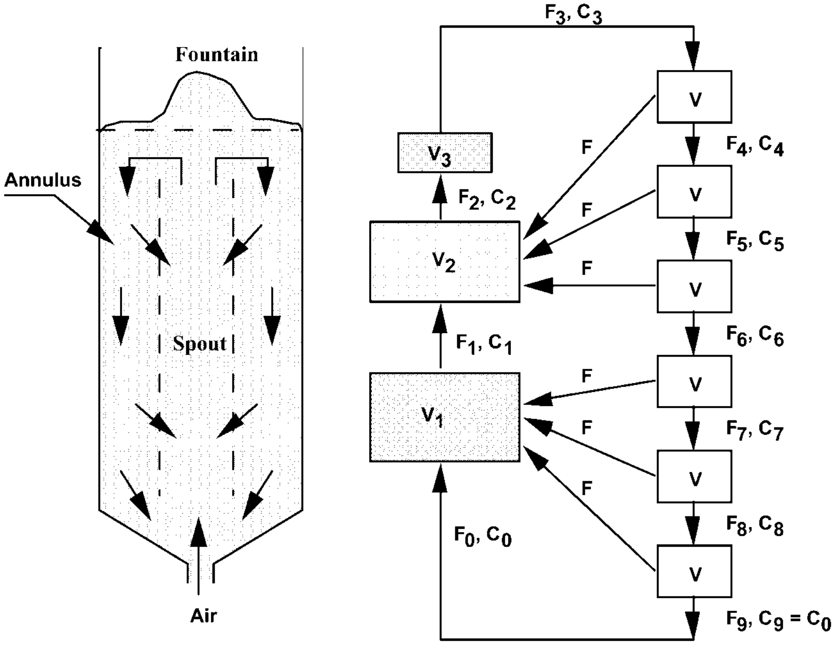


Fig. 1 The spouted bed and its mixing model.

Experimental tracer studies are to be carried out in which the solid in the bottom half of the bed is initially mixed with tracer, the bed started and timed samples taken from various locations in the bed annular region. It is desired to model the resulting tracer distribution in the bed in order to find the fractional slippage rate between the annular tanks and the central bed regions.

Model

The initial expansion of the bed consequent to the start of the air flow is neglected from the analysis. Component balance equations for each region of the reactor are given.

For the bed central flow region

$$V_1 \frac{dC_1}{dt} = F_0 C_0 + F[C_7 + C_8 + C_9] - F_1 C_1$$

$$V_2 \frac{dC_2}{dt} = F_1 C_1 + F[C_4 + C_5 + C_6] - F_2 C_2$$

$$V_3 \frac{dC_3}{dt} = F_2C_2 - F_3C_3$$

For the annular flow region

$$V \frac{dC_4}{dt} = F_3C_3 - [F_4 + F]C_4$$

$$V \frac{dC_5}{dt} = F_4C_4 - [F_5 + F]C_5$$

$$V \frac{dC_6}{dt} = F_5C_5 - [F_6 + F]C_6$$

$$V \frac{dC_7}{dt} = F_6C_6 - [F_7 + F]C_7$$

$$V \frac{dC_8}{dt} = F_7C_7 - [F_8 + F]C_8$$

$$V \frac{dC_9}{dt} = F_8C_8 - [F_9 + F]C_9$$

where $F_1 = F_0 + 3\ F$
$F_2 = F_1 + 3\ F$
$F_3 = F_2$
$F_4 = F_3 - F$
$F_5 = F_4 - F$
$F_6 = F_5 - F$
$F_7 = F_6 - F$
$F_8 = F_7 - F$
$F_9 = F_8 - F$

and $C_0 = C_9$

Total bed volume

$$V_{Total} = V_1 + V_2 + V_3 + 6V$$

The initial distribution of tracer within the bed is represented by

At $t = 0$, $C_0 = C_1 = C_7 = C_8 = C_9 = C_{Start}$

$C_2 = C_3 = C_4 = C_5 = C_6 = 0$

Program

If desired, the model and program can be extended by adding a continuous inlet and outlet stream and by incorporating the E-curve methods found in Example CSTRPULSE.

Nomenclature

Symbols

V	Volume	m^3
F	Volumetric flow rate	m^3/h
C	Tracer concentration	mg/m^3

Indices

0, 1,...9	Refer to designated regions and flow rates (see Fig. 1).

Exercises

1. Determine the time required for the tracer to be nearly completely mixed throughout the vessel. Which criterion did you use for uniform mixing?
2. Change the initial conditions to place the tracer at a different region of the vessel. Does this effect the time for complete mixing?
3. Double the flowrates in the vessel, and note the influence on the time for mixing.

Results

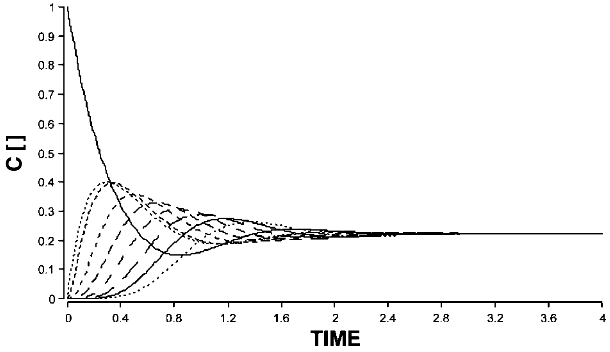


Fig. 2 A pulse in compartment 1 mixes with all the compartments in about 3 h.

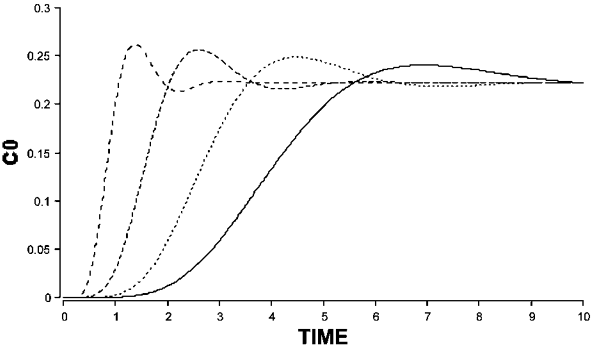


Fig. 3 As expected, a 10 fold change in F0 from 0.1 to 1.0 m^3/s causes a similar difference in the mixing times.

5.6.6
BATSEG, SEMISEG and COMPSEG – Mixing and Segregation in Chemical Reactors

System

Chemical reactions will take place only when the reactant molecules are in intimate contact. In some cases, especially with very fast reactions or viscous liquids, segregation of the reactants can exist, which make the reaction rates and selectivities dependent on the mixing intensity. In chemical reactor engineering, the assumption is usually made that only mean concentrations need be considered. In reality, concentration values fluctuate about a mean, and in some cases these fluctuations must be considered in detail. This field is very complex and is still the subject of much research. This example serves only to introduce these concepts and to show how simulations can be made for certain simple situations.

The concept of segregation and its meaning to chemical reactors was first described by Danckwerts (1953). The intensity or degree of segregation is given the symbol I, which varies between one and zero. Shown in Fig. 1 is a tank with two components, A and B, which are separated into volume fractions, q_A and $1-q_A$; this condition represents complete initial segregation ($I=1$). Stirring or

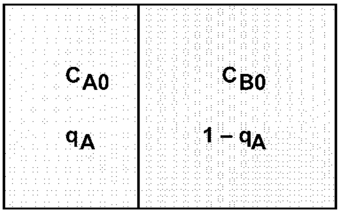


Fig. 1 Complete segregation ($I=1$) of reactants A and B in two volume fractions.

mixing this tank would cause the segregation to decay until complete homogeneity would be achieved ($I=0$). In this situation, the rate of any reaction between the reactants could obviously be influenced by the rate of mixing, as measured by the change in I.

Segregation may also be important if the reactants are fed to a reactor in an unmixed condition. This could be the case in any continuously fed reactor, either tubular (Fig. 2) or tank (Fig. 3).

The intensity of segregation, I, can be described in terms of concentration fluctuations, as shown in Fig. 4. Here the time-varying fluctuations above and below an average value are shown.

Fig. 2 Feeding of unmixed reactants to a tubular reactor.

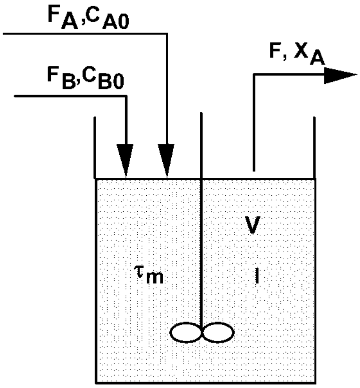


Fig. 3 Unmixed reactants fed into a continuous stirred tank.

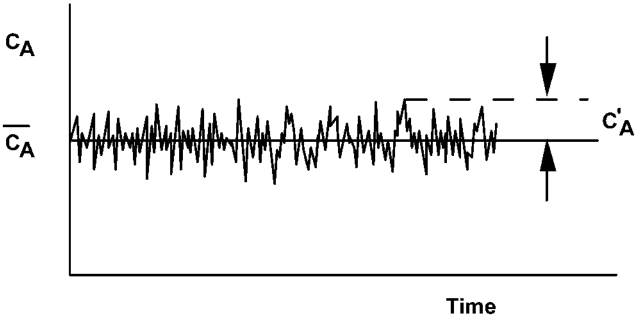


Fig. 4 Time-variant turbulent fluctuations of concentration about a mean value ($\overline{C_A}$), showing the fluctuation value C'_A.

The unmixedness can be characterised by the mean of the square of the fluctuations or concentration variance, according to

$$\overline{C_A'^2} = \overline{(C_A - C_A)^2}$$

To compare the “state of unmixedness”, Danckwerts introduced the intensity of segregation, which is calculated in terms of the mean square of the fluctuations, as

$$I = \frac{\overline{C_A'^2}}{\left\lfloor \overline{C_A'^2} \right\rfloor_0}$$

where the subscript 0 denotes the initial or feed value.

In the case shown in Fig. 1, the initial mean square fluctuations would be

$$\left\lfloor \overline{C_A'^2} \right\rfloor_0 = C_{A0}^2 \overline{q_A}(1 - \overline{q_A})$$

For unpremixed feed streams, the mean volume fraction is defined in terms of the mean entering flow rates as

$$\overline{q_A} = \frac{\overline{F_A}}{\overline{F_A} + \overline{F_B}}$$

Segregation or unmixedness of non-reactive systems, as measured by I or $\left\lfloor \overline{C_A'^2} \right\rfloor$, can be balanced using the general macroscopic population balance equation as follows

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of unmixedness} \\ \text{in the system} \end{pmatrix} = \begin{pmatrix} \text{Flow of} \\ \text{unmixedness} \\ \text{into} \\ \text{the system} \end{pmatrix} - \begin{pmatrix} \text{Flow of} \\ \text{unmixedness} \\ \text{out of} \\ \text{the system} \end{pmatrix}$$

$$\begin{pmatrix} \text{Dissipation rate} \\ \text{of unmixedness} \\ \text{by mixing} \\ \text{in the system} \end{pmatrix} + \begin{pmatrix} \text{Rate of} \\ \text{production} \\ \text{of unmiedness} \\ \text{in the system} \end{pmatrix}$$

The dissipation rate term, r_{dm}, can be taken as a first-order decay of concentration variance whose rate constant is the inverse mixing time

$$r_{dm} = -\frac{1}{\tau m} \overline{C_A'^2}$$

The mixing time can be related to power per unit volume and the geometry. Turbulent dispersion can produce unmixedness within the system, if there are gradients of mean concentration. This is not considered here. A useful discussion of these equations was given by Brodkey (1975) and Baldyga (1989). This area is treated in a recent book by Baldyga and Bourne (1999).

Model

In what follows, the above balance for unmixedness is applied to individual reactor cases. The relation for reaction rate in terms of I is then considered, and finally this is applied for simple and complex reactions.

Intensities of Segregation in a Batch Reactor

For a batch reactor system only the accumulation and dissipation terms are important. Thus

$$V\frac{d(\overline{C_A'^2})}{dt} = -\frac{1}{\tau_m}\overline{C_A'^2}V$$

With the initial value of $\left\lfloor \overline{C_A'^2} \right\rfloor_0$, integration gives

$$\frac{\overline{C_A'^2}}{\lfloor \overline{C_A'^2} \rfloor_0} = I = e^{-t\tau_m}$$

This equation predicts the intensity of segregation to decay with time in the batch reactor. It is also applicable to a steady-state plug flow system, where t is the residence time.

Intensities of Segregation in a Continuous Reactor

For a steady-state continuous tank reactor only the flow terms and the dissipation terms are important. Thus

$$0 = F\left\lfloor \overline{C_A'^2} \right\rfloor_0 - F\overline{C_A'^2} - \frac{1}{\tau_m}\overline{C_A'^2}V$$

With the mean residence time $\tau = V/F$, this becomes

$$\frac{\overline{C_A'^2}}{\left\lfloor \overline{C_A'^2} \right\rfloor_0} = I = \frac{1}{1 + \tau/\tau_m} = \frac{\tau_m/\tau}{1 + \tau_m/\tau} = \frac{\Theta_m}{\Theta_m + 1}$$

where $\Theta_m = \tau_m/\tau$.

Intensities of Segregation in a Semi-Continuous Reactor

In a semi-batch system the volume varies from zero to V_{max} with total flow rate F as

$$\frac{dV}{dt} = F_A + F_B = F$$

or for constant F

$$V = Ft$$

During filling, the accumulation, inflow and dissipation terms are important. Thus the balance gives

$$\frac{dI}{dt} = \frac{1 - I}{t} - \frac{I}{\tau_m}$$

where feed and the initial tank contents are completely segregated, i.e., $I(0) = 1$.

Introducing dimensionless time, $\Theta = t/\tau$, and dimensionless mixing time, $\Theta_m = \tau_m/\tau$, during the filling period ($\Theta < 1$) gives

$$\frac{dI}{d\Theta} = \frac{1 - I}{\Theta} - \frac{I}{\Theta_m}$$

After the reactor is full and overflowing $V = V_{max}$, and therefore $\tau = V_{max}/F$. Then $\Theta \geq 1$ and the outflow term is also important. The balance becomes

$$\frac{dI}{d\Theta} = 1 - I - \frac{I}{\Theta_m}$$

Reaction Rate in Terms of Intensity of Segregation

The rate of a simple $A + B \rightarrow C$ reaction, which is given by the instantaneous concentrations is expressed in terms of the mean concentrations and the extra variable $\overline{C'_A}\,\overline{C'_B}$, becoming

$$\overline{r_A} = -kC_A C_B = -k\left(\overline{C_{A0}}\,\overline{C_{B0}} + \overline{C'_A}\,\overline{C'_B}\right)$$

The derivation of this rate expression depends on the theory developed by Toor (1969) and assumes that with and without reaction the covariances of the reactant fluctuations are the same, as given by

$$\overline{C'_A}\,\overline{C'_B} = -I\left(\overline{C_{A0}}\,\overline{C_{B0}}\right)$$

Mixing effects are particularly important for complex reactions, since selectivity is changed. The following reaction is considered

$$A + B \xrightarrow{k_1} R \qquad \text{(desired reaction)}$$

$$R + B \xrightarrow{k_2} S \qquad \text{(undesired reaction)}$$

The kinetics in terms of the intensities of segregation and the mean concentrations can be shown to be

$$\overline{r_A} = -k\left(\overline{C}_A\,\overline{C}_B - I\overline{C_{A0}}\,\overline{C_{B0}}\right)$$

$$\overline{r_B} = -k_1(\overline{C}_A\overline{C}_B - I\overline{C_{A0}}\,\overline{C_{B0}}) - k_2\overline{C_B}\,\overline{C_R}$$

$$\overline{r_R} = +k_1(\overline{C}_A\overline{C}_B - I\overline{C_{A0}}\,\overline{C_{B0}}) - k_2\overline{C_B}\,\overline{C_B}$$

$$\overline{r_S} = +k_2\overline{C_B}\,\overline{C_B}$$

This result was obtained by Toor and Bourne (1977) by neglecting the influence of the covariance, $C'_B C'_R$ and by assuming that $C'_A C'_B$ could be estimated by Toor's hypothesis, as explained above. This simplification is restricted to a relatively slow second reaction and to a volume ratio q_A/q_B near one.

Batch Reactor

The batch reactor balance for a simple $A + B \rightarrow C$ reaction becomes

$$\frac{d(\overline{C_A})}{dt} = \overline{r_A} = -k(\overline{C_A}\,\overline{C_B} - I\overline{C_{A0}}\,\overline{C_{B0}})$$

Dimensionless variables can be defined as follows: $\Theta = t/\tau_m$, $\eta = \overline{C_{B0}}/\overline{C_{A0}}$, $Da = k\overline{C_{A0}}\tau$, and $y = \overline{C_A}/\overline{C_{A0}}$. Here $\overline{C_{B0}} = C_{B0}q_B/(q_A+q_B)$ and $\overline{C_{A0}} = C_{A0}q_A/(q_A+q_B)$. The dimensionless balance becomes

$$\frac{dy}{d\Theta} = -Da[y(y + \eta - 1) - I\eta] = -Da[y(y + \eta - 1) - e^{-\Theta}\eta]$$

where the initial value $y(0) = 1$.

For finite y, when $Da \rightarrow \infty$ this gives

$$[y(y + \eta - 1) - I\eta] \rightarrow 0$$

and thus y_∞ is given by the quadratic formula

$$y_\infty = \frac{-(\eta - 1) \pm \sqrt{(\eta - 1)^2 + 4\eta I}}{2}$$

In this case only the + sign has a physical meaning.

The conversion X in the batch tank is given by $X = 1 - y$, which becomes

$$\frac{dX}{d\Theta} = Da[(1 - X)(\eta - X) - I\eta] = Da[(1 - X)(\eta - X) - e^{-\Theta}\eta]$$

The above equations also apply to a plug flow reactor, where Θ is the dimensionless residence time, which varies with distance.

Continuous Stirred-Tank Reactor

For a simple $A + B \rightarrow C$ reaction in a continuous stirred-tank reactor, as shown in Fig. 3, in terms of fraction conversion of the reactant A, the balance becomes

$$X = Da[(1 - X)(\eta - X) - I\eta]$$

with the fractional conversion defined as

$$X = 1 - \frac{\overline{C_A}}{\overline{C_{A0}}}$$

where $\overline{C_{A0}} = C_{A0}\ F_A/(F_A + F_B)$

If X is to be finite when $Da \rightarrow \infty$, the term $[(1–X)\ (\eta–X)–I\,\eta] \rightarrow 0$, and then as before

$$X_\infty = \frac{(1 + \eta) \pm \sqrt{(1 + \eta)^2 - 4\eta(1 - I)}}{2}$$

since $0 < X_\infty < 1$, only the minus sign has meaning here.

Generally

$$X = \frac{\left(1 + \eta + \frac{1}{Da}\right) \pm \sqrt{\left(1 + \eta + \frac{1}{Da}\right)^2 - 4\eta(1 - I)}}{2}$$

Semi-Batch Reactor

For a simple A + B → C reaction the semi-batch reactor balance is

$$\frac{d(\overline{C_A})}{dt} = \frac{F}{V}(\overline{C_{A0}} - \overline{C_A}) - k(\overline{C_A}\,\overline{C_B} - I\overline{C_{A0}}\,\overline{C_{B0}})$$

using the same dimensionless quantities, this becomes

$$\frac{dy}{d\Theta} = \frac{1}{A}(1 - y) - Da[y(y + \eta - 1) - I\eta]$$

with $y(0) = 1$. Here the constant $A = \Theta$ during the filling period, and $A = 1$ after the filling period, when $\Theta > 1$.

The requirement to have y finite when $Da \to \infty$ gives

$$y_\infty = \frac{-(\eta - 1) \pm \sqrt{(\eta - 1)^2 + 4\eta I}}{2}$$

The component balances for the complex reaction

$$A + B \xrightarrow{k_1} R \qquad \text{(desired reaction)}$$

$$R + B \xrightarrow{k_2} S \qquad \text{(undesired reaction)}$$

become as follows:

A-balance

$$\frac{d(\overline{C_A})}{dt} = \frac{F}{V}(\overline{C_{A0}} - \overline{C_A}) - k_1(\overline{C_A}\,\overline{C_B} - I\overline{C_{A0}}\,\overline{C_{B0}})$$

B-balance

$$\frac{d(\overline{C_B})}{dt} = \frac{F}{V}(\overline{C_{B0}} - \overline{C_B}) - k_1(\overline{C_A}\,\overline{C_B} - I\overline{C_{A0}}\,\overline{C_{B0}}) - k_2\overline{C_B}\,\overline{C_R}$$

R-balance

$$\frac{d(\overline{C_R})}{dt} = -\frac{F}{V}\overline{C_R} + k_1(\overline{C_A}\,\overline{C_B} - I\overline{C_{A0}}\,\overline{C_{B0}}) - k_2\overline{C_B}\,\overline{C_R}$$

S-balance

$$\frac{d(\overline{C}_S)}{dt} = -\frac{F}{V}\overline{C}_S + k_2\overline{C}_B\overline{C}_R$$

During the filling period $V < V_{max}$.

When combined with the total balance with constant F, the dimensionless form of these equations apply both to the filling and full periods. These are

$$\frac{dy_A}{d\Theta} = \frac{1}{A}(1 - y_A) - \beta\,Da(y_A y_B - I\eta)$$

$$\frac{dy_B}{d\Theta} = \frac{1}{A}(\eta - y_B) - \beta\,Da(y_A y_B - I\eta) - Da\,y_B y_R$$

$$\frac{dy_R}{d\Theta} = -\frac{1}{A}y_R + \beta\,Da(y_A y_B - I\eta) - Da\,y_B y_R$$

$$\frac{dy_S}{d\Theta} = -\frac{1}{A}y_S + Da\,y_B y_R$$

where the dimensionless terms are $\Theta = t/\tau$, $\eta = \overline{C_{B0}}/\overline{C_{A0}}$, $Da = k_2\overline{C_{A0}}\tau$, $y = \overline{C_i}/\overline{C_{A0}}$ and $\beta = k_1/k_2$. Here $\tau = V/F$, and the feed concentrations are $y_{A0} = 1$, $y_{B0} = h$, $y_{R0} = 0$ and $y_{S0} = 0$. During the filling period $A = \Theta$, and $A = 1$ when $\Theta > 1$. For the desired selectivity, $\beta = k_1/k_2 > 1$, and $\eta < 1$.

Selectivity at any time Q can be defined as:

$$X_S = \frac{2y_S}{y_R + 2y_S}$$

Here a value of $X_S = 1$ would mean that no desired product was obtained.

Program

The programs are as follows: BATSEG for a simple batch reactor, SEMISEG for a semi-continuous reactor that fills up and becomes continuous and COMPSEG for the complex reaction in a semi-continuous reactor. This example was developed by J. Baldyga., Dept. of Chem. and Proc. Eng., Warsaw University of Technology, Poland.

Nomenclature

Symbols

C	Concentration	kmol/m^3
$\overline{C_A'^2}$	Concentration fluctuation variance	kmol^2/m^6
Da	Damköhler number (= $k\overline{C_{A0}}\tau$ and $k_2\overline{C_{A0}}\tau$)	–
F	Volumetric flow rate	m^3/s
I	Degree of segregation	–
q	Fractional flow rate	–
t	Time	s
V	Volume	m^3
X	Fractional conversion	–
y	Dimensionless concentration	–
β	Ratio of reaction rate constants ($=k_1/k_2$)	–
η	Initial concentration ratio ($=\overline{C}_{B0}/\overline{C}_{A0}$)	–
Θ	Dimensionless time ($=t/\tau$) or ($=\tau/\tau_m$)	–
τ	Time constant or mean residence time	s

Indices

$'$	Refers to fluctuations around mean value
0	Refers to initial or input value
dm	Refers to dissipation of unmixedness
m	Refers to mixing
max	Refers to maximum volume
T	Refers to tank
∞	Refers to Da = infinity
$\overline{}$	Refers to mean value

Exercises

1. Very high values of Da correspond to instantaneous reactions. Verify that simulations with BATSEG and SEMISEG give results corresponding to the quadratic formulae presented.
2. Show by simulation that the corresponding conversion of B for instantaneous reaction is given by solving the equation $(1-X)(\eta-X)-I\eta=0$
3. Investigate the influence of concentration ratio, η, from 0.05 to 0.8 on the selectivity and concentration of desired product using COMPSEG.
4. With all three programs, vary the Damköhler number, Da, over a range from 1 to 500 and explain the results. Note that when Da no longer has any influence on the rate, then mixing must be controlling.

Results

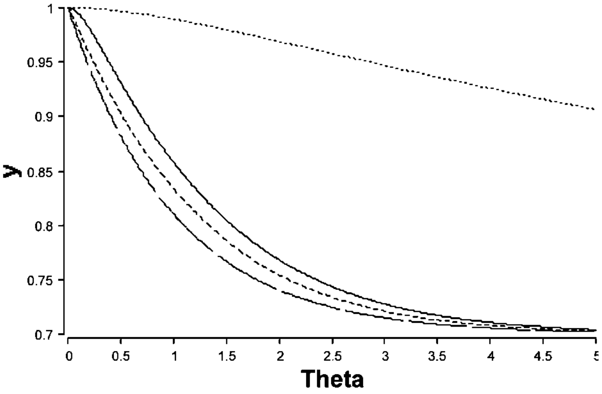


Fig. 5 Program BATSEG: Dimensionless concentration y versus dimensionless time Θ for Da=0.1, 5.0, and 100. Shown also is the decay of segregation I with time.

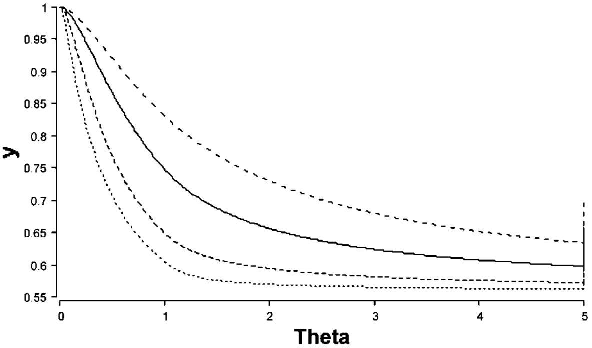


Fig. 6 Program SEMISEG: Varying THETAMIX (0.03, 0.1, 0.3 and 0) gave these results for the semi-batch reactor. Note that when THETA reaches 1.0 the reactor is full and becomes continuous.

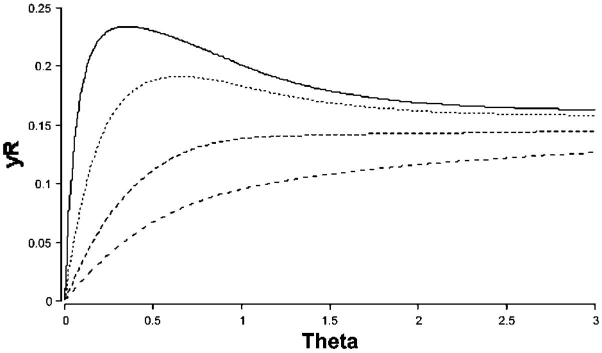


Fig. 7 Program COMPSEG: Dimensionless concentration of desired product YR versus dimensionless time THETA obtained by varying THETAMIX (0.03, 0.1, 0.3, and 0.6. Parameter values used: ETA = 0.3, BETA = 2000, DA = 1.0.

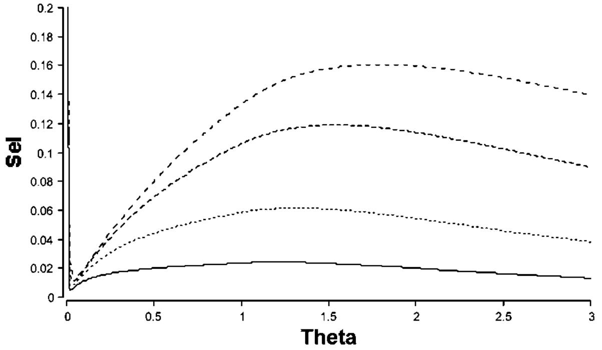


Fig. 8 Selectivity SEL profiles corresponding to the simulations in Fig. 7. Low values of SEL are desired. Mixing is seen to greatly influence the selectivity, even though the second reaction is much slower.

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