

## 5 Simulation Tools and Examples of Chemical Engineering Processes

In this chapter the simulation examples are presented. They are preceded by a short description of simulation tools and the MADONNA program in particular. As seen from the Table of Contents, the examples are organised according to thirteen application areas: Batch Reactors, Continuous Tank Reactors, Tubular Reactors, Semi-Continuous Reactors, Mixing Models, Tank Flow Examples, Process Control, Mass Transfer Processes, Distillation Processes, Heat Transfer, Biological Process Examples and Environmental Process Examples. There are aspects of some examples that make them relevant to more than one application area, and this is usually apparent from their titles. Within each section, the examples are listed in order of their degree of difficulty.

Each simulation example is identified by a section number, a file name and a title, and each comprises the qualitative physical description with a drawing, the model equation development, the nomenclature, exercises, sample graphical results and literature references. A few selected examples have the BERKELEY-MADONNA program in the text. The CD in the pocket at the back of the book contains all the programs and the MADONNA software versions for Windows and MAC OSX. Guidance for running a MADONNA program is given in the Appendix, in the form of both a simplified manual and a screenshot guide. The Help section of MADONNA should also be consulted.

The objective of the exercises with each example is, of course, to aid in understanding the example physical and mathematical models. Usually changes in parameters are suggested, which can either be accomplished by the use of overlay plots and sliders or by multiple runs. Some exercises involve making minor changes in a program statement, some require adding a few lines to the program and some even require writing a new self-standing program. Since the MADONNA version on the CD is not registered, it is not possible to save any modified programs or new programs directly. However, any modified programs can still be run. The CD contains registering information for the full modestly priced shareware to be made available to the reader.

The reader-simulator should try to relate the simulation results to the parameters used and to the model equations. For this understanding, it is necessary to refer back to the model equations and to the program. Most users will find it useful to make notes of the parameters investigated and to sketch the expected graphical results before they are obtained by simulation.

## 5.1 Simulation Tools

### 5.1.1 Simulation Software

Many different digital simulation software packages are available on the market. Modern tools are numerically powerful, highly interactive and allow sophisticated types of graphical and numerical output. Many packages also allow optimisation and parameter estimation.

A small selection of available software is given in Table 5.1. MADONNA is very user-friendly and is used in this book. This recent version has a facility for parameter estimation and optimisation. MODELMAKER is also a more recent powerful and easy to use program, which also allows optimisation and parameter estimation. ACSL has quite a long history of application in the control field, and also for chemical reaction engineering.

Both MATLAB and ASCL include powerful algorithms for non-linear optimisation, which can also be applied for parameter estimation. Optimisation and parameter estimation are also discussed in greater detail in Sections 2.4.1 and 2.4.2.

#### Software Links

A large compilation of information on the many simulation software tools is available on the Internet at [www.idsia.ch/%7Eandrea/sim/simtools.html](http://www.idsia.ch/%7Eandrea/sim/simtools.html).

**Table 5.1** Software Examples

Program	Computer	Characteristics
BERKELEY MADONNA	PC and Mac	Easy to use, powerful, highly interactive, easy and effective parameter estimation and optimisation.
MODELMAKER	PC	Easy to use, graphical model representation, parameter estimation and optimisation.
ACSL- OPTIMIZE	PC	Powerful mathematics, building blocks especially for control purposes, includes powerful and user-friendly optimisation and parameter estimation.
MATLAB- SIMULINK	All types	Powerful mathematical package especially for linear problems includes optimisation routines, powerful integration routines, model building blocks and graphical interface.
HYSYS and SPEEDUP	PC and larger	Dynamic and steady-state simulation of large processes with data base.

For the software of particular interest here, refer to the following websites: BERKELEY MADONNA, [www.berkeleymadonna.com](http://www.berkeleymadonna.com); MODELMAKER, [www.modelkinetix.com/modelmaker/](http://www.modelkinetix.com/modelmaker/); MATLAB, <http://www.mathworks.com>; ACSL, <http://www.aegisxcellon.com/>; HYSYS and SPEEDUP <http://www.aspentec.com>

### 5.1.2

#### Teaching Applications

The solution technique, based on the use of a simulation language, is particularly beneficial in teaching, because it permits easy programming, easily comprehensible program listings, a rapid and efficient solution of the model equations, interaction with the model and a convenient graphical output of the computed results. In our experience, digital simulation has proven itself to be the most effective way of introducing and reinforcing new concepts which involve multiple interactions.

### 5.1.3

#### Introductory MADONNA Example: BATSEQ-Complex Reaction Sequence

The complex chemical reaction, shown below, is carried out in an isothermal, constant-volume, batch reactor. All the reactions follow simple first-order kinetic rate relationships, in which the rate of reaction is directly proportional to concentration (Fig. 1).

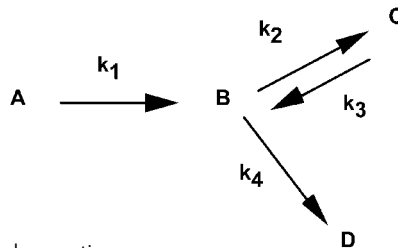


Fig. 1 Example of a complex reaction sequence.

The model equations for each component of this system are

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B + k_3 C_C - k_4 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B - k_3 C_C$$

$$\frac{dC_D}{dt} = k_4 C_B$$

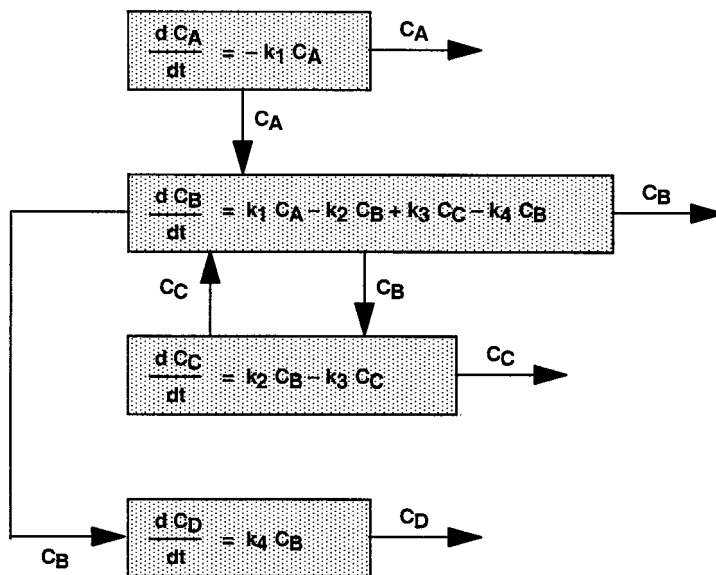


Fig. 2. Information flow diagram for the complex reaction model equations.

where  $C_A$ ,  $C_B$ ,  $C_C$  and  $C_D$  are the concentrations of components, A, B, C and D, respectively and  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are the respective kinetic rate coefficients.

If the number of equations is equal to the number of unknowns, the model is complete and a solution can be obtained. The easiest way to demonstrate this is via an information flow diagram as shown in Fig. 2.

It is seen that all the variables, required for the solution of any one equation block are obtained as results from other blocks. The information flow diagram thus emphasises the complex interrelationship of this very simple problem.

#### BERKELEY-MADONNA Program BATSEQ

MADONNA provides an effective means of solving very large and complicated sets of simultaneous non-linear ordinary differential equations. The above complex reaction problem is solved with considerable ease by means of the following MADONNA program, which is used here to illustrate some of the main features of solution.

```

{Example BATSEQ}
{COMPLEX BATCH REACTION SEQUENCE}

METHOD AUTO
DT = 0.1
STOPTIME= 500 {Time period of simulation, sec.}

K1 = 0.01 {First order rate constant, 1/s}
K2 = 0.01 {First order rate constant, 1/s}
K3 = 0.05 {First order rate constant, 1/s}
K4 = 0.02 {First order rate constant, 1/s}

INIT CA=1 {Initial concentration, kmol/m3}
INIT CB=0 {Initial concentration, kmol/m3}
INIT CC=0 {Initial concentration, kmol/m3}
INIT CD=0 {Initial concentration, kmol/m3}

{Balance equations for components A, B, C and D}
d/dt (CA) = rA
d/dt (CB) = rB
d/dt (CC) = rC
d/dt (CD) = rD

{Kinetic rate terms for components A, B, C and D }
rA = -K1*CA
rB = K1*CA-K2*CB+K3*CC-K4*CB
rC = K2*CB-K3*CC
rD = K4*CB

MOLE = CA+CB+CC+CD {Sum of moles}

```

Note that the program does not have to have a pre-specified structure, although it is useful for purposes of program clarity, to group like items together. Here the first two program lines are used to describe the file name and title of the program and are bounded by the brace brackets to show that they represent non-executable program statements. The next three lines concern the integration specifications and there are discussed in more detail later. The following four lines are used to give the values of the kinetic rate constants K1 to K4. These are then followed by the initial conditions for each of the four model variables, CA, CB, CC, and CD, using the Madonna prefix of INIT.

The initial structure of the program is then followed by statements reflecting the dynamic model equations. These are also provided with comment lines with surrounding braces to distinguish them from the executable program lines. Note that the kinetic rate equations are expressed separately apart from the balance equations, to provide additional simplicity and additional flexibility. The kinetic rates are now additional variables in the simulation and the rates can

also be plotted for further study. Note also the direct relationship between each individual program statement and the corresponding model equation.

Finally, an algebraic model relationship is included in order to check on the total component material balance achieved in the simulation. The last lines specify the chemical reaction rate terms and calculate the total number of moles present at any time during the reaction.

All the variables appearing on the left-hand side of the program equations are evaluated by the computer, during the simulation and are thus all available for graphing. The derivative notation  $d/dt(CA)$  denotes a differential equation, requiring the application of a numerical integration procedure for its solution. Here line 3 of the program specifies the Madonna integration method AUTO, as the means of solution. Numerical integration of all the differential equations comprising the model commences from their initial conditions, as specified by lines 10 to 13, and from an initial time. This may be specified by STARTTIME, but is usually taken by default as being equal to 0. Note that the numerical integration proceeds in parallel with all the model variables being updated simultaneously, at the end of each integration step length, with the integration continuing up to the final time of the simulation, set by STOPTIME as specified by line 5. Line 4 determines the increment of time DT within some of the integration routines. Each routine has its own set of parameters, as seen in the **Parameter/Parameter Window**. A too high value of DT can result in a failure of the integration. Too low a value of DT may slow the speed of integration and also generate an unduly high quantity of numerical data, which can be compensated by setting an appropriate value for DTOUT.

The program BATSEQ is available on the CD, with this book, but can be copied to an alternative hard disk location, or placed on diskette. The following steps represent a usual run procedure:

1. Open the file BATSEQ and examine the model equations, using the **Model/Equations** menu.
2. Specify a new graph with **Graph/New Window** and the variables to be used with **Graph/Choose Variables**. Click on **RUN** and the plot will be made.
3. If the run fails to produce satisfactory values, this may be due to the choice of an inappropriate integration method or an inappropriate choice of the integration parameters of DT, DTMAX or DTMIN. Changes in these parameters can then be best achieved by use of the **Parameters/Parameter Window**. Here any other parameter values for the problem can also be changed. Note that when viewing the value of the parameters in this window, a \* before a particular value indicates a changed value from that specified in the program. Clicking on **Reset** will restore the original value.
4. Changing the value of say K1 and clicking on **RUN** will enable a second simulation, based on the changed value of the parameter to be obtained. Note that it may also be necessary to change the value of STOPTIME, to accord either with a shorter or longer run time.

5. Run a few changes again but first click the **O Button** on the graph to obtain an overlay plot. In this way, each run for each new value of K1 will be plotted on top of the previous runs and thus providing an easy means of comparing the effects of system parameter changes.
6. Sliders can also be used to conveniently change parameters. This can be done by going to **Parameters/Define Sliders** and choosing the parameter and its desired range. Each time the value of the slider parameter is slid to a new value, a run will be made and the results will be graphed, which can be done either separately or as an overlay plot.
7. A series of runs can be made automatically for a range of parameter values by choosing **Parameters/Batch Runs**. The parameter, to be changed, is then defined together with the number of runs and the range of values required. All the results of the runs will then be plotted together.
8. For a multiple run graph, click on the **Lock Button** above the graph window. Otherwise the new multiple run will not ask for a new window and the first runs will be lost.
9. Other useful buttons on the graph window are **Table output, Legend, Parameters, Colours, Dashed Lines, Data Points, Grid, Readout** and **Zoom**.
10. The axis scales can be rearranged to plotting variables on either the left and right hand side of the graph, as chosen in **Graph/Choose Variables**. TIME is always displayed on the X axis as the default condition, but any calculated value can be chosen.

The Screenshot Guide in the Appendix provides a full explanation for the major features of BERKELEY-MADONNA and the mechanics of running the simulation examples. The Help menu of MADONNA should also be consulted.

## 5.2

## Batch Reactor Examples

## 5.2.1

## BATSEQ – Complex Batch Reaction Sequence

## System

The following complex reaction sequence can be used to study various reaction kinetics of interest simply by varying the rate constants.

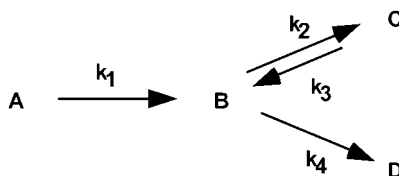


Fig. 1. A complex reaction sequence.

## Model

For batch kinetics the model equations become

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B + k_3 C_C - k_4 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B - k_3 C_C$$

$$\frac{dC_D}{dt} = k_4 C_B$$

For this batch reaction case, the sum of all the mols must equal the initial mols charged.



**Program**

Part of the program is given below.

```
{Batch mass balances for components A, B, C and D }
d/dt (CA) = rA
d/dt (CB) = rB
d/dt (CC) = rC
d/dt (CD) = rD
{Kinetic rate terms for components A, B, C and D}
rA=-K1*CA
rB=K1*CA-K2*CB+K3*CC-K4*CB
rC=K2*CB-K3*CC
rD=K4*CB
```

**Nomenclature****Symbols**

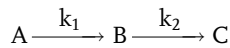
C	Component concentration	kmol/m <sup>3</sup>
k	First-order reaction rate constant	1/s
t	Time	s

**Indices**

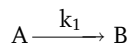
1, 2, 3, 4	Refer to reactions
A, B, C, D	Refer to components

**Exercises**

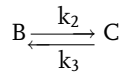
- Study the effect of varying rate coefficients  $k_1, k_2, k_3, k_4$  in the range (0.001 to 0.1) on the time-dependent concentrations of A, B, C and D. Note that  $C_B$  and  $C_C$  pass through maximum values.
- Set  $k_3 = k_4 = 0$ , to simulate a simple consecutive reaction sequence.



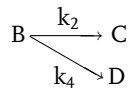
- Set  $k_2 = k_3 = k_4 = 0$ , to simulate a simple first-order reaction.



4. Set the initial values for  $C_A = C_C = C_D = 0$ ,  $C_B = 1$  and  $k_1 = k_4 = 0$ , to simulate a simple first-order reversible reaction.



5. Note that when using the initial conditions of Exercise 4 but with  $k_1 = k_3 = 0$ , the program models a simple first-order parallel reaction sequence.



6. Write the model and program in terms of mole fractions.
7. BATSEQ is also one of the first examples that is also of interest to study from the waste minimisation viewpoint. As suggested in Section 2.5, this can be achieved by means of incorporating a simple weighting or cost factor for each material to account for positive sales value, negative cost values representing unused or excess reactants and negative penalty cost values representing the potential damage of the waste to the environment. Regarding B and C to be useful products and D to be harmful waste, modify the program to define appropriate cost values (\$/kmol) for each compound and define a total environmental cost function. Hence find the optimum reaction time producing the minimum environmental cost and compare this value to that simply based on the maximum concentration of B or C. Vary the relative cost values and study the sensitivity of the process to the harmful nature of the waste.

## Results

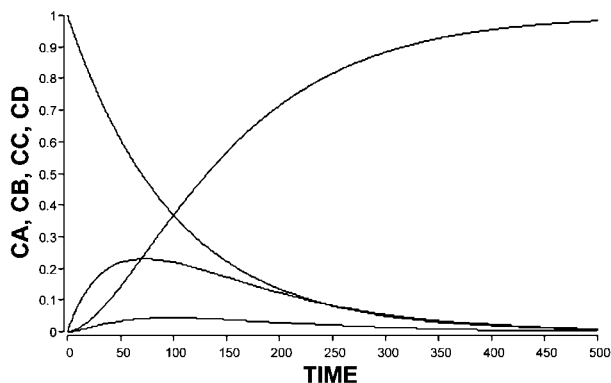


Fig. 2. Profiles of concentrations versus time as obtained from the rate constants in the program.

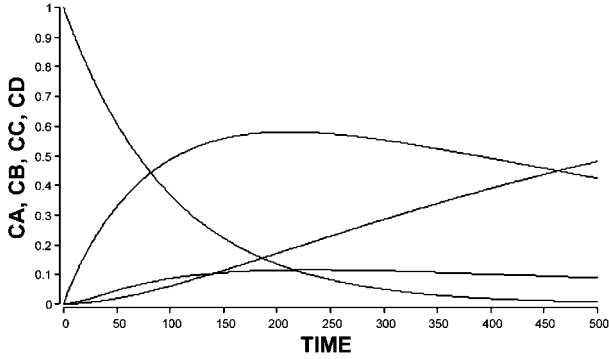


Fig. 3. Changing  $K_4$  from 0.02 to 0.002 resulted in these profiles, otherwise the same constants as Fig. 2.

### 5.2.2

#### BATCHD – Dimensionless Kinetics in a Batch Reactor

##### System

An  $n$ th-order homogeneous liquid phase reaction is carried out in a batch tank reactor.

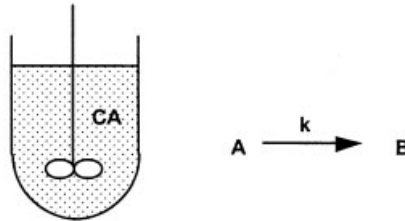


Fig. 1. Batch reactor with simple  $n$ -th order reaction

##### Model

The batch balance for the reactant A with  $n$ th-order kinetics is

$$V \frac{dC_A}{dt} = -k C_A^n V$$

Dimensionless variables are defined as

$$\bar{C}_A = \frac{C_A}{C_{A0}}$$

$$\bar{t} = t k C_{A0}^{n-1}$$

where  $C_{A0}$  is the initial concentration.

The dimensionless balance equation is then

$$\frac{d\bar{C}_A}{d\bar{t}} = -\bar{C}_A^n$$

In this form the results are independent of  $k$ .

## Nomenclature

### Symbols

$C_A$	Concentration of A	kmol/m <sup>3</sup>
$\bar{C}_A$	Dimensionless concentration of A	–
$C_{A0}$	Initial concentration of A	kmol/m <sup>3</sup>
$k$	Reaction rate constant	m <sup>3(n-1)</sup> /kmol <sup>(n-1)</sup> s
$n$	Reaction order	–
$t$	Time	s
$\bar{t}$	Dimensionless time	–
$V$	Volume	m <sup>3</sup>

### Exercises

1. For a first-order reaction  $n = 1$ , the dimensionless time is given by the value of  $[kt]$ . Make a series of runs with different initial concentrations and compare the results, plotting the variables in both dimensional and dimensionless terms.
2. For  $n = 2$  the dimensionless time is  $[ktC_{A0}]$ . Make the runs and study the results as in Exercise 1. Verify that a change in  $k$  and a change in  $C_{A0}$  have the same influence as long as the product term  $kC_{A0}$  is maintained constant.
3. The sensitivity of the reaction is given by the order of reaction,  $n$ . Experiment with this, changing  $n$  in the range 0 to 3.

### Results

Dimensionless and normal output variables are plotted below.

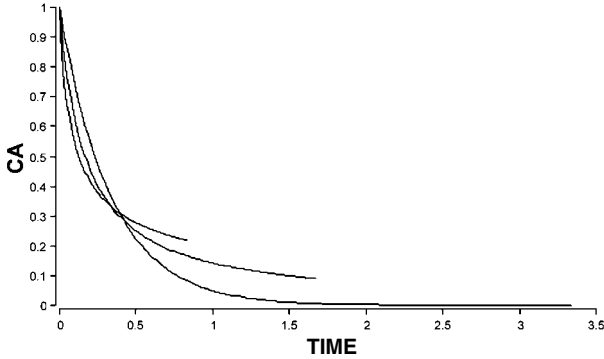


Fig. 2. Profile of dimensionless concentration of A versus dimensionless time for  $n=1, 2,$  and  $3$ .  $CA_0=2$ .

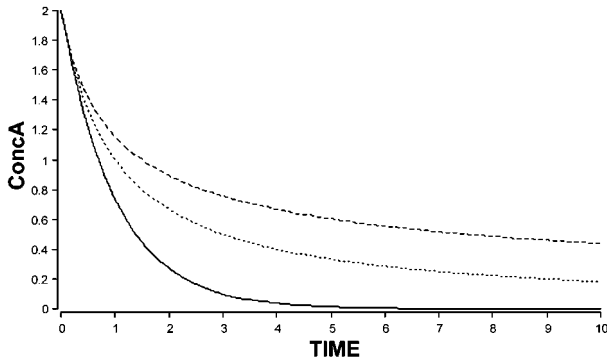


Fig. 3. Profile of concentration A versus time for the same parameters as in Fig. 2.

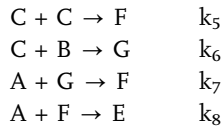
### 5.2.3

#### COMPREAC – Complex Reaction

##### System

The complex batch reaction between formaldehyde, A, and sodium *p*-phenol sulphonate, B, proceeds in accordance with the following complex reaction scheme. All the reactions follow second-order kinetics. Components C, D and F are intermediates, and E is the final product.

Reaction	Rate Coefficient
$A + B \rightarrow C$	$k_1$
$A + C \rightarrow D$	$k_2$
$C + D \rightarrow E$	$k_3$
$B + D \rightarrow F$	$k_4$



### Model

For a constant volume batch reaction, the balance equations for each component lead to

$$\frac{dC_A}{dt} = -k_1 C_A C_B - k_2 C_A C_C - k_7 C_A C_G - k_8 C_A C_F$$

$$\frac{dC_B}{dt} = -k_1 C_A C_B - k_4 C_B C_D - k_6 C_C C_B$$

$$\frac{dC_C}{dt} = k_1 C_A C_B - k_2 C_A C_C - k_3 C_C C_D - 2k_5 C_C^2 - k_6 C_C C_B$$

$$\frac{dC_D}{dt} = k_2 C_A C_C - k_3 C_C C_D - k_4 C_B C_D$$

$$\frac{dC_E}{dt} = -k_3 C_C C_D + k_8 C_A C_F$$

$$\frac{dC_F}{dt} = k_4 C_B C_D + k_5 C_C^2 + k_7 C_A C_G - k_8 C_A C_F$$

$$\frac{dC_G}{dt} = k_6 C_C C_B - k_7 C_A C_G$$

### Nomenclature

#### Symbols

C	Concentration	kmol/m <sup>3</sup>
k	Rate coefficient	m <sup>3</sup> /kmol min
R	Rate	kmol/ m <sup>3</sup> min

#### Indices

A, B, ..., G	Refer to components
1, 2, ..., 8	Refer to reactions

## Exercises

1. Vary the initial concentrations of the reactants A and B and observe their effect on the relative rates of the individual reactions and on the resulting product distribution. Note how the distribution varies with time.
2. Write the model in dimensionless form, program it and compare the results with those from Exercise 1.

## Results

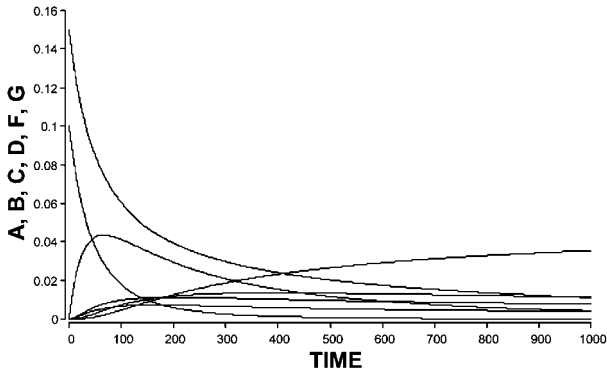


Fig. 1. Concentration-time profiles using the parameters as given in the program

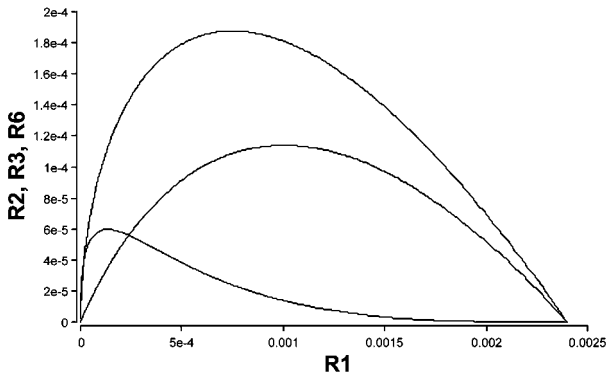


Fig. 2. Phase-plane plot showing variation of  $R_2$ ,  $R_3$  and  $R_6$  versus  $R_1$ .

## Reference

Stults, F.C., Moulton, R.W. and McCarthy, J.L. (1952) Chem. Eng. Prog. Symp. Series, Vol. 4, 38.

## 5.2.4

**BATCOM – Batch Reactor with Complex Reaction Sequence****System**

Product B is manufactured by the liquid phase batch reaction, whose complexity gives a range of byproducts.

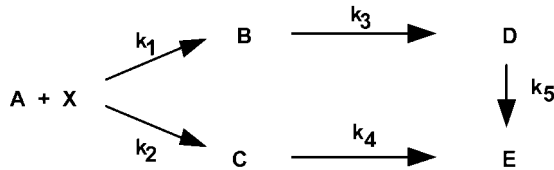


Fig. 1. This complex reaction can be altered to fit various situations.

The batch reactor can be run in the temperature range 180 to 260 C. Reactant X is in large excess, and C, D, and E are undesired byproducts.

The reactions follow first-order relationships, where,

$$r = -kC$$

and

$$k = Ze^{-E_a/RT}K$$

**Model**

For the batch reactor with these complex kinetics, the batch balances are as follows

$$\frac{dC_A}{dt} = -(k_1 + k_2)C_A$$

$$\frac{dC_B}{dt} = k_1C_A - k_3C_B$$

$$\frac{dC_C}{dt} = k_2C_A - k_4C_C$$

$$\frac{dC_D}{dt} = k_3C_B - k_5C_D$$

$$\frac{dC_E}{dt} = k_4C_C + k_5C_D$$



**Program**

The program can be used to generate repeated runs for differing values of reactor temperature  $T_C$ . The range of interest is 180 to 260°C.

**Nomenclature****Symbols**

C	Concentration	kmol/m <sup>3</sup>
$E_a$	Activation energy	kJ/kmol
k	Reaction rate constant	1/s
R	Gas constant	kJ/kmol K
t	Time	s
$T_K$	Reactor temperature	K
$T_C$	Reactor temperature	°C
Z	Arrhenius constant	1/s

**Indices**

A, B, C, D, E Refer to components  
1, 2, 3, 4, 5 Refer to reactions

**Exercises**

1. Determine the optimum batch time and batch temperature giving maximum yield of B.
2. Under optimum conditions, determine the concentrations of A, B, C, D and E obtained.
3. Check your results with the following analytical solution

$$C_A = e^{-(k_1+k_2)t}$$

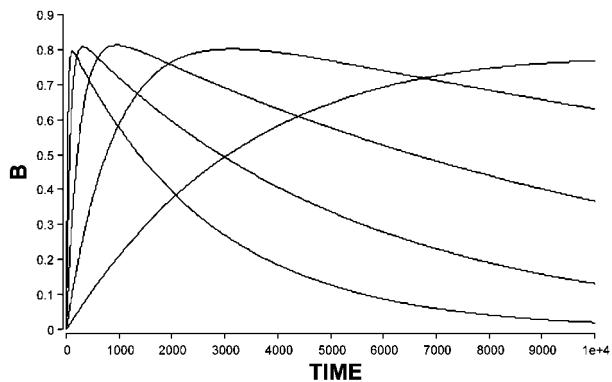
$$C_B = \frac{k_1}{k_1 + k_2 - k_3} (e^{-k_3t} - e^{-(k_1+k_2)t})$$

$$C_C = \frac{k_2}{k_1 + k_2 - k_4} (e^{-k_4t} - e^{-(k_1+k_2)t})$$

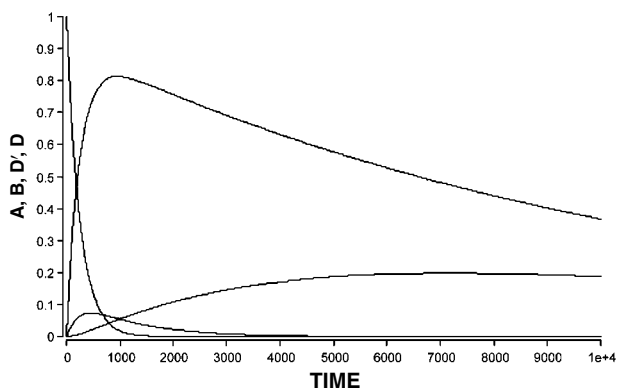
Note: These equations can be easily programmed using MADONNA.

4. Introduce a new variable  $r_B$  describing the net formation rate of B. Use parametric runs to determine the batch time and batch temperature for maximum B formation.

## Results



**Fig. 2.** Profiles of B versus time for a range of reactor temperatures, TC, from 180 to 260 K, curves A to E. The optimum corresponds to TR = 220 (middle curve).



**Fig. 3.** Profiles of concentrations for TC = 220.

## Reference

Binns, D. T., Kantyka, K. A. and Welland, R. C. (1969) *Trans. Inst. Chem. Engrs.* 47, 53.

## 5.2.5

**CASTOR – Batch Decomposition of Acetylated Castor Oil****System**

The batch decomposition of acetylated castor oil to drying oil proceeds via the following reaction:

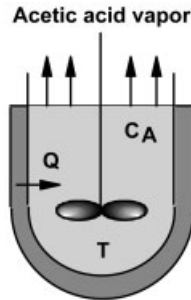


Fig. 1. The reactor for CASTOR, showing acetic acid vapour escaping.

The reaction is endothermic, and heat transfer to the reactor is required in order to accomplish the decomposition of the acetylated oil and to liberate acetic acid vapour. The example has been considered previously by Smith (1972), Cooper and Jeffreys (1971) and Froment and Bischoff (1990). Data values are based on those used by Froment and Bischoff.

**Model**

With respect to the material balances, the solution here treats the process as occurring with variable reactor mass because of the loss of acetic acid vapour.

The rate of production of acetic acid (kg acid/kg charge s)

$$r_p = k C_A$$

Here  $C_A$  is the equivalent mass fraction of acetyl, and the rate constant varies with  $T$  as

$$k = \frac{1}{60} \exp\left(35.2 - \frac{22450}{T}\right)$$

The acetic acid vaporizes immediately, and the total balance is

$$\frac{dM}{dt} = -m_{\text{vap}}$$

where

$$m_{\text{vap}} = r_p M$$

The acetyl component balance for variable total mass conditions is given by

$$\frac{d(MC_A)}{dt} = -r_p M$$

where

$$C_A = \frac{MC_A}{M}$$

and the fraction conversion is

$$X_A = 1 - \frac{MC_A}{M_0 C_{A0}}$$

According to the derivation given in Section 1.2.5 the energy balance equation is

$$M c_p \frac{dT}{dt} = -r_p M \Delta H + Q$$

where the heat of reaction,  $\Delta H$ , includes the vaporisation of acetic acid.

### Program

The simplicity of the Madonna program should be compared with the solutions in the literature. PID control has been added to the program to control the heat to the reactor. To turn off the control set  $K_p = 0$ . Then  $Q$  will be equal to  $Q_1$ , i.e., the base heating rate.

### Nomenclature

#### Symbols

$C_A$	Equivalent acetic acid content	kg/kg
$C_{A0}$	Initial equivalent acetic acid content	kg/kg
$c_p$	Specific heat	kJ/kg K
$\Delta H$	Heat of reaction with vaporisation	kJ/kg

k	Kinetic rate constant	1/s
M	Total mass of castor oil charge	kg
M <sub>0</sub>	Initial total mass of castor oil charge	kg
Q	Heat input	kJ/s
r <sub>p</sub>	Rate of production of acetic acid	kg/kg s
T	Reactor temperature	K
t	Time	s

### Exercises

1. Study the effect of differing rates of heat input on the fractional conversion  $X$  and reactor temperature  $T$ , for the range  $Q = 0$  to 200 kJ/s, and note particularly the effect on the reactor time required to obtain a given conversion efficiency.
2. Repeat Exercise 1 for differing batch starting temperatures.
3. In your simulations, plot temperature and conversion versus time and also plot temperature versus fractional conversion.
4. Calculate the temperature drop for adiabatic operation from the equation.

$$M C_{A0} \Delta H = M C_p \Delta T_{\text{adiab.}}$$

Verify this by simulation.

5. Try to operate the reactor isothermally with the PID-control as programmed to control the heat input rate.
6. Add a first order time delay function to the heater to give a more realistic situation. Experiment with the control settings and compare the results with and without the heater delay.

### Results

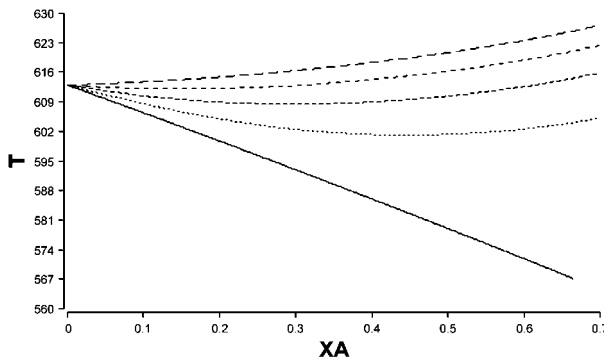


Fig. 2. Temperature versus fractional conversion obtained by setting  $Q = 0$ , 40, 80, 120 and 160 kJ/s.

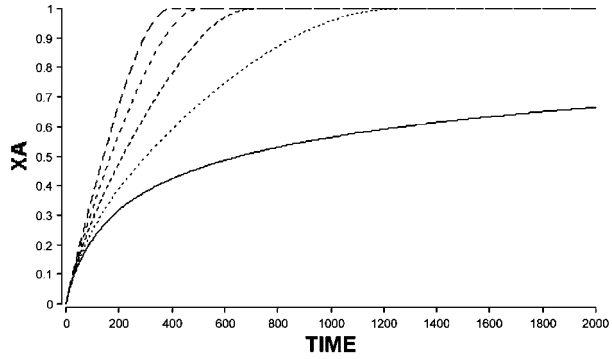


Fig. 3. Conversion-time profiles corresponding to Fig. 2.

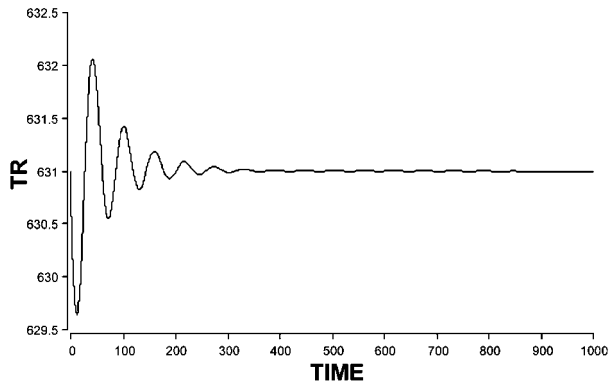


Fig. 4. Temperature profile with PID-control.  $K_p = 4.35$ ,  $\tau_{I,INT} = 0.21$ ,  $\tau_{A,DER} = 6.2$ ,  $\Delta t = 0.01$

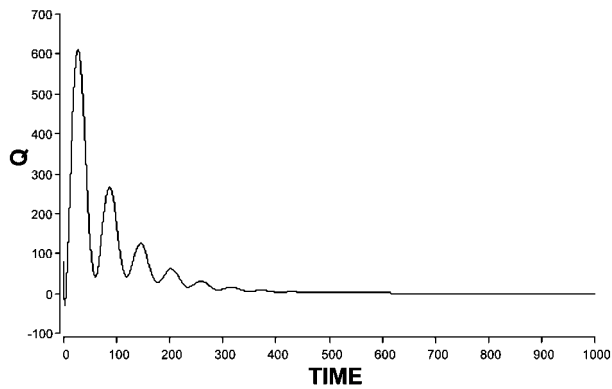


Fig. 5. Heat input with PID-control corresponding to Fig. 4

## References

- Smith (1972) Chemical Engineering Kinetics., McGraw-Hill, Vol. 2.  
 Cooper and Jeffreys (1971) Chemical Kinetics and Reactor Design, Chem Engr. Texts.  
 Froment, G. F. and Bischoff, D. B. (1990) Chemical Reactor Analysis and Design. 2nd edition, Wiley.

### 5.2.6

#### HYDROL – Batch Reactor Hydrolysis of Acetic Anhydride

##### System

The liquid phase hydrolysis reaction of acetic anhydride to form acetic acid is carried out in a constant volume, adiabatic batch reactor. The reaction is exothermic with the following stoichiometry

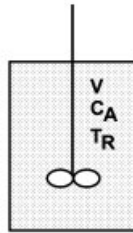


Fig. 1. The adiabatic batch reactor with variables of concentration and temperature.

##### Model

The acetic anhydride balance can be formulated as

$$\left( \begin{array}{c} \text{Rate of accumulation} \\ \text{in reactor} \end{array} \right) = \left( \begin{array}{c} \text{Rate of loss due to} \\ \text{chemical reaction} \end{array} \right)$$

hence, for the first-order reaction

$$\frac{d(\text{VC}_A)}{dt} = -k\text{C}_A V$$

and for constant volume conditions

$$\frac{d\text{C}_A}{dt} = -k\text{C}_A$$

The fractional conversion for the batch is

$$X_A = \frac{C_{A0} - C_A}{C_{A0}}$$

The temperature influence on the rate is given by

$$k = Z e^{-E/RT} R$$

The heat balance under adiabatic conditions is as follows:

$$\left( \begin{array}{l} \text{Rate of accumulation} \\ \text{of heat in the reactor} \end{array} \right) = \left( \begin{array}{l} \text{Rate of heat generation} \\ \text{by chemical reaction} \end{array} \right)$$

$$M c_p \frac{dT_R}{dt} = -k C_A V \Delta H$$

or

$$\frac{dT_R}{dt} = -k C_A V \frac{\Delta H}{M c_p}$$

## Nomenclature

### Symbols

$C_A$	Concentration of A	$\text{kmol/m}^3$
$C_{A0}$	Initial concentration of A	$\text{kmol/m}^3$
$c_p$	Specific heat	$\text{kJ/kg K}$
$E$	Activation energy	$\text{kJ/kmol}$
$\Delta H$	Heat of reaction	$\text{kJ/kmol}$
$k$	Rate constant	$1/\text{s}$
$M$	Mass in tank	$\text{kg}$
$R$	Gas constant	$\text{kJ/kmol K}$
$T_R$	Temperature in reactor	$\text{K}$
$V$	Volume of charge	$\text{m}^3$
$X$	Fractional conversion	–
$\rho$	Solution density	$\text{kg/m}^3$

## Exercises

1. Study the effect of differing initial batch charge temperatures on the fractional conversion  $X_A$ , the reactor temperature  $T_R$ , and the required batch time.
2. What initial temperature is required to give 99% conversion if the batch temperature must not exceed 300 K? What is the corresponding batch time required?



3. What is the batch time requirement for the reactor operating isothermally at 20 C. How must the heat removal requirement vary during the batch in order to maintain the batch temperature constant?

### Results

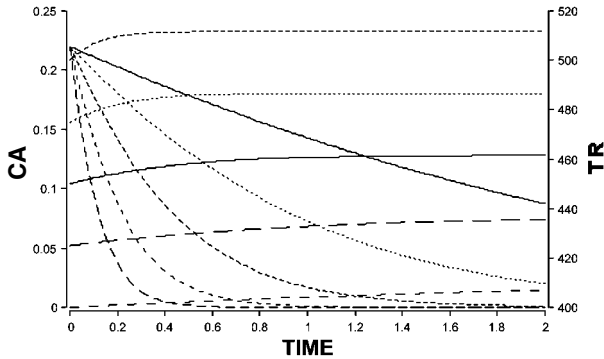


Fig. 2 Temperature and concentration variations with time for a range of starting temperature,  $TR_0$ .

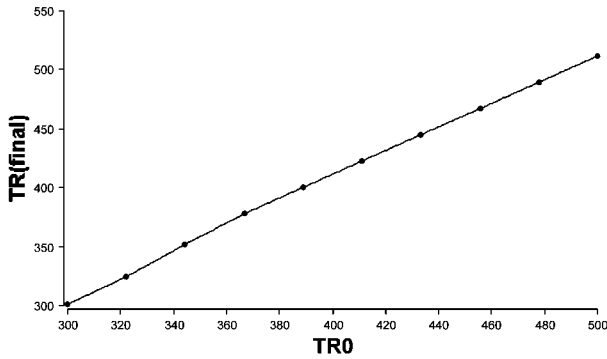


Fig. 3. Variation of fraction conversion during the runs in Fig. 2.

### Reference

Cooper, A. R. and Jeffreys, G. V. (1971) Chemical Kinetics and Reactor Design, Chem. Engng. Texts, 133.

## 5.2.7

**OXIBAT – Oxidation Reaction in an Aerated Tank****System**

To be investigated are the influences of gassing rate and stirrer speed on an oxidation reaction in an aerated batch reactor. The outlet gas is assumed to be of normal air composition, which eliminates the need of a balance for the well-mixed gas phase, since the gas oxygen composition does then not change.

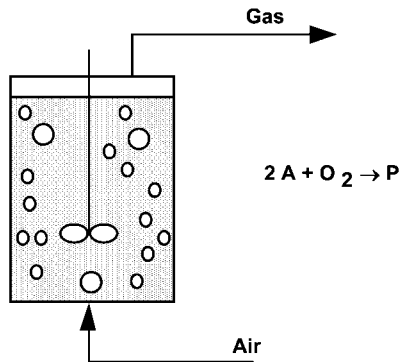


Fig. 1. Schematic drawing of the batch enzymatic oxidation reactor.

**Model**

The reaction kinetics are described by a second-order relation in reactant A and oxygen

$$r_A = -k_r C_A C_O$$

The stoichiometry gives

$$r_O = \frac{1}{2} \cdot r_A$$

$$r_P = -\frac{1}{2} \cdot r_A$$

The batch mass balances are

$$V \frac{dC_A}{dt} = r_A V$$

$$V \frac{dC_O}{dt} = K_L a (C_O^* - C_O) V + r_O V$$

$$V \frac{dC_P}{dt} = r_P V$$

$K_{L,a}$  varies with stirring speed ( $N$ ) and aeration rate ( $G$ ) according to

$$K_{L,a} = k_t N^3 G^{0.5}$$

where  $k_t = 23.8$  with  $N$  in  $1/s$ ,  $G$  in  $m^3/s$  and  $K_{L,a}$  in  $1/s$ .

## Nomenclature

### Symbols

$C_O$	Dissolved oxygen concentration	$kmol/m^3$
$C_O^*$	Saturation oxygen concentration	$kmol/m^3$
$G$	Aeration rate	$m^3/s$
$K_{L,a}$	Transfer coefficient	$1/s$
$k$	Second-order rate constant	$m^3/kmol \cdot s$
$k_t$	Constant in $K_{L,a}$ correlation	$s^{2.5}/m^{1.5}$
$N$	Stirring rate	$1/s$
$P$	Product concentration	$kmol/m^3$
$r$	Reaction rate	$kmol/m^3 \cdot s$

### Indices

- 0 Refers to feed
- A Refers to reactant
- O Refers to oxygen
- P Refers to product

### Exercises

1. Vary the stirrer speed  $N$  and aeration rate  $G$  and observe the response in dissolved oxygen  $C_O$  and product concentration  $C_P$ .
2. Vary the system operating parameters in the very low  $C_O$  range ( $2 \cdot 10^{-6} \text{ kmol/m}^3$ ) and note the influence on the rates.
3. Graph the oxygen transfer rate and verify that the rate of reaction is limited by oxygen transfer.
4. Calculate the value of  $K_{L,a}$  required to give  $C_O = C_O^*/2$  when  $C_A = 0.2$ . Verify by simulation.
5. Reduce the aeration rate until the reaction becomes oxygen-limited. Maintain this and then reduce the catalyst amount by  $1/2$  (reduce  $k_r$  by one-half). Does the initial rate decrease by  $1/2$ ? Is the reaction still oxygen-limited?

6. Run the process oxygen-limited and observe the increase of  $C_O$  at the end of the reaction.
7. Increase  $N$  by 25% and notice the change of  $K_L a$  and  $C_O$ .
8. Vary  $N$  and  $G$  under non-oxygen-limiting conditions. What is the effect on the reaction rate?

## Results

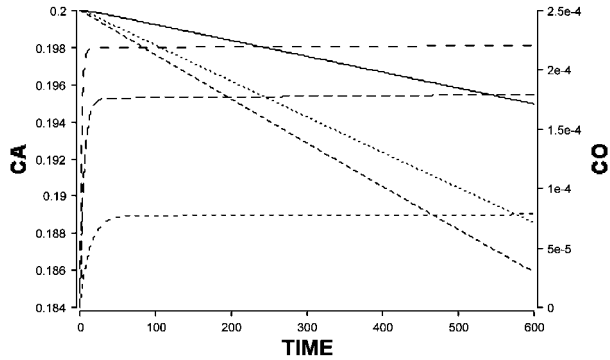


Fig. 2. Response of dissolved oxygen and reactant concentration for three stirrer speeds.

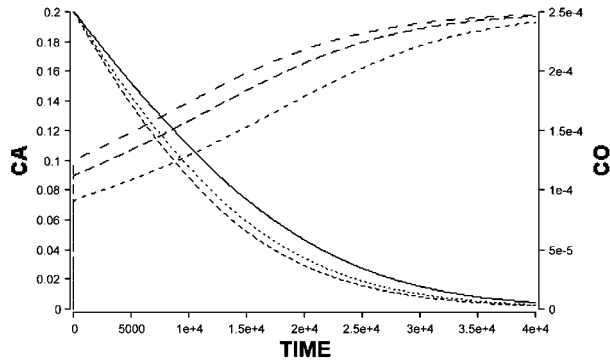


Fig. 3. Response of  $C_A$  and  $C_O$  profiles with different gassing rates until the reactant  $C_A$  is consumed.

## 5.2.8

## RELUIY – Batch Reactor of Luyben

## System

The first-order consecutive exothermic reaction sequence,  $A \rightarrow B \rightarrow C$ , is carried out in a thick-walled, jacketed batch reactor, provided with both jacketed heating and cooling, as shown below.

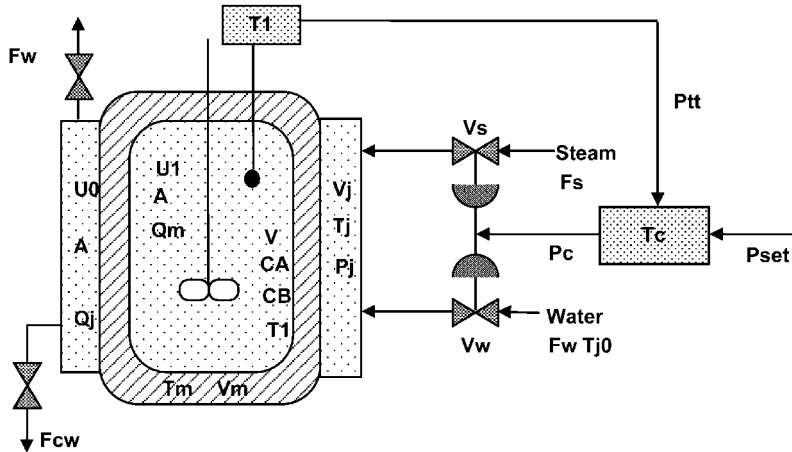


Fig. 1. Batch reactor with temperature control, adding steam and water via a split-range valve to the reactor jacket.

The reactants are charged and the contents heated by steam up to the starting batch temperature via the split range valve  $V_s$ . Steam to the jacket is supplied until the reactor temperature,  $T_1$ , reaches the maximum allowable temperature  $T_{max}$  when the steam flow is then stopped. With cooling control,  $T_{max}$  is held for a time period and then a linear ramp cooling follows. The cooling water is supplied to the jacket via the split range valve  $V_w$  at a controlled rate, set in accordance with a prescribed temperature–time profile, by a controller cam operating on the set point.

Component B is the desired product of the reaction, and the aim is to find the optimum batch time and temperature to maximise the selectivity for B. Saturated steam density data are taken from steam tables and fitted to a polynomial. The model and data for this example are taken from Luyben (1973).

**Model**

The balances for the reactor liquid are as follows:

Total mass balance, assuming constant density

$$\frac{d(\rho V)}{dt} = 0$$

Thus  $V = \text{constant}$ .

Component balances,

$$V \frac{dC_A}{dt} = -V k_1 C_A$$

$$V \frac{dC_B}{dt} = V k_1 C_A - V k_2 C_B$$

where

$$k_1 = Z_1 e^{-E_1/RT}$$

and

$$k_2 = Z_2 e^{-E_2/RT}$$

The reactor energy balance is

$$\rho V c_p \frac{dT}{dt} = -V k_1 C_A (-\Delta H_1) + V k_2 C_B (-\Delta H_2) - U_1 A (T - T_m)$$

The energy balance for the metal wall at constant  $c_p$  is

$$\rho_m V_m c_{pm} \frac{dT_m}{dt} = U_1 A (T_1 - T_m) - U_s A (T_m - T_j)$$

For both heating and cooling, the energy balance remains the same except that differing values of the overall heat transfer coefficient now apply. Thus for the coolant  $U_s$  is replaced by  $U_c$ .

A mass balance for the jacket is used to calculate the temperature of the saturated steam.

$$V_j \frac{d\rho_s}{dt} = F_s - F_{cw}$$

From steam table relations

$$T_j = f(\rho_s)$$

$$P_j = (1/14.5) * \exp\left(\frac{K_A}{T_j + K_B}\right)$$

During the cooling period, the energy balance for the jacket is

$$V_j c_{pw} \rho_w \frac{dT_j}{dt} = F_w c_{pw} \rho_w (T_{j0} - T_j) + U_c A (T_m - T_j)$$

The steam valve is initially opened slowly by increasing  $X_s$  from 0 to 1 and then kept open until the reactor temperature,  $T_1$ , reaches  $T_{1\max}$ . Then it is closed and the temperature is controlled at  $T_{1\max}$  for time  $\text{TIME}_{\text{hold}}$ . Then the cooling ramp is started.

The temperature transmitter has a range of 283 to 390 K and an output 0.2 to 1 bar. Hence,

$$P_{tt} = 0.2 + (T_1 - 283)K_{PT}$$

where  $K_{PT}$  is a constant.

For the proportional feedback controller

$$P_c = P_0 + K_c(P_{\text{set}} - P_{tt})$$

The set point for the water ramp cooling is given by

$$P_{\text{set}} = P_{\text{set0}} - K_{\text{ramp}}(\text{TIME} - (\text{TIME}_{\text{st}} + \text{TIME}_{\text{hold}}))$$

where  $\text{TIME}_{\text{st}}$  is the time when the reactor temperature first reaches a temperature  $T_{\max}$ , and  $\text{TIME}_{\text{hold}}$  is the time period to maintain  $T_{\max}$  constant.

### Program

The Madonna program makes use of conditional statements to distinguish between the heating and cooling periods: This is done by switching values of the conditional variables HEAT and COOL, to take values of either 0 or 1 in order to switch the heating or cooling on or off. Heating is accomplished with steam at a mass flow rate of  $F_s$ . The material balance for the steam jacket determines the steam density  $\rho_s$ , which, together with a steam table function, determines the temperature of the steam in the jacket  $T_j$ . A root finding routine in Madonna is used to set the initial density of the steam in the jacket.

When the reactor temperature  $T_1$  becomes greater than the maximum,  $T_{\max}$ , the values of the conditional variables switch to HEAT = 0 and COOL = 1, such that the program turns the cooling water on with a mass flow rate of  $F_w$ . This flow is controlled by a proportional controller with control constant  $K_c$ . The set point for the controller ( $P_{\text{set}}$ ) is varied according to a time ramp function with a constant  $K_{\text{ramp}}$ . The output of the controller to the control valve is  $P_c$ . The ramp set point remains constant until time period  $\text{TIME}_{\text{hold}}$  has passed. Then the setpoint is decreased linearly. The temperature is sensed using a pressure transmitter with output  $P_{tt}$ . The conditional logic is further described in the program.

**Nomenclature**

A	Heat transfer area of jacket	$m^2$
C	Concentration	$kmol/m^3$
$c_p$	Specific heat of vessel contents	$kJ/kg\ K$
$c_{pm}$	Specific heat of metal wall	$kJ/kg\ K$
$c_{pw}$	Specific heat of cooling water	$kJ/kg\ K$
$C_{vs}$	Valve constant for steam	$kg/s\ (bar)^{0.5}$
$C_{vw}$	Valve constant for water	$m^3/s\ (bar)^{0.5}$
$E_i$	Activation energy of reaction	$kJ/mol$
$F_s$	Steam flow rate	$kg/s$
$F_w$	Cooling water rate	$m^3/s$
$F_{cw}$	Condensed water flow rate	$m^3/s$
$k_i$	Reaction rate constant	$1/s$
$K_A$	Constant in steam pressure relation	K
$K_B$	Constant in steam pressure relation	–
$K_C$	Controller constant	–
$K_{ramp}$	Ramping constant	$bar/s$
$P_0$	Controller pressure	$bar$
$P_c$	Controller pressure output	$bar$
$P_j$	Steam vapour pressure	$bar$
$P_{j0}$	Steam supply pressure	$bar$
$P_{Set}$	Set point pressure	$bar$
$P_{tt}$	Pressure of temperature transmitter	$bar$
$P_{w0}$	Water supply pressure	$bar$
R	Gas constant	$kJ/kmol\ K$
$T_1$	Temperature in reactor	K
$T_{1abs}$	Absolute reactor temperature	K
$T_j$	Temperature of jacket contents	K
$T_{j0}$	Steam supply temperature	K
$T_m$	Temperature of metal wall	K
$T_{w0}$	Water supply temperature	K
$T_{1max}$	Temperature for batch start	K
$TIME_{st}$	Time when $T_{1max}$ is first reached	s
$TIME_{hold}$	Time period to hold $T_{1max}$	s
$U_1$	Heat transfer coeff. contents to wall	$kJ/s\ m^2\ K$
$U_w$	Heat transfer coeff. wall to coolant	$kJ/K\ s\ m^2$
$U_s$	Heat transfer coeff. wall to steam	$kJ/K\ s\ m^2$
V	Vessel volume	$m^3$
$V_j$	Jacket volume	$m^3$
$V_m$	Wall volume	$m^3$
$X_s$	Steam valve position	–
$X_w$	Water valve position	–
$Z_i$	Arrhenius rate constant	$1/s$



$\Delta H_1$	Reaction enthalpy	kJ/mol
$\lambda$	Latent heat of steam	kJ/kg
$\rho$	Density of vessel contents	kg/m <sup>3</sup>
$\rho_j$	Density of steam in jacket	kg/m <sup>3</sup>
$\rho_s$	Steam supply density	kg/m <sup>3</sup>
$\rho_m$	Density of wall	kg/m <sup>3</sup>
$\rho_w$	Density of cooling water	kg/m <sup>3</sup>

### Indices

- A Refers to component A
- B Refers to component B
- 0 Refers to inlet
- 1 Refers to reaction A  $\rightarrow$  B
- 2 Refers to reaction B  $\rightarrow$  C

### Exercises

- Vary the temperature of the heating period limit,  $T_{\max}$ , and note the influence on the concentration profiles.
- Study the effects of the parameters of the cooling water ramp function ( $\text{TIME}_{\text{hold}}$  and Kramp) on the selectivity defined in the program as

$$\text{SEL} = \frac{C_B - C_{B0}}{C_{A0} - C_A}$$

- Investigate the influence of the wall mass and the heat transfer coefficients on the maximum yield of B.

### Results

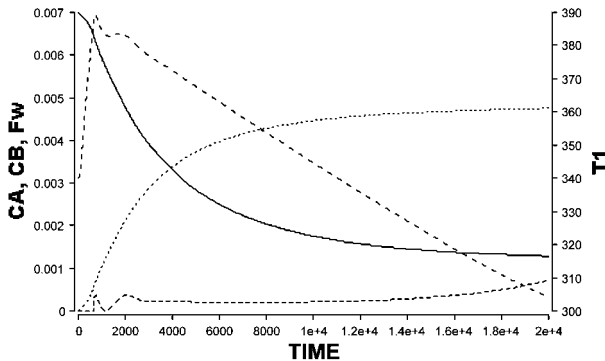


Fig. 2. A run with  $\text{TIME}_{\text{hold}} = 3000$  s showing the variation of temperature, cooling water flowrate, and concentrations of A and B.

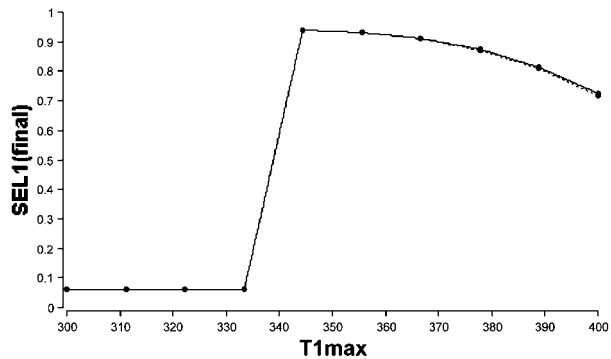


Fig. 3. A “parametric run” varying T1max to obtain the selectivity at the end of the run.

## Reference

Luyben, W.L. (1973) *Process Modeling, Simulation, and Control for Chemical Engineers*, McGraw-Hill.

### 5.2.9

## DSC – Differential Scanning Calorimetry

### System

Differential scanning calorimetry (DSC) is a method for measuring the heat effects and temperature stability of reactants with a small scale experiment. Keller et al. (1997) used dynamic simulation to investigate screening methods for the thermal risk of chemical reactions using this method. In this example, the measurement of heat production rate of a consecutive reaction ( $A \rightarrow B \rightarrow C$ ) using DSC is modelled. The sample is filled into the reaction crucible, while a second crucible serves as reference. The experiment is started by slowly increasing the oven temperature. During the process of decomposition caused by the high temperatures, the temperature difference between the two crucibles is measured. As seen by the simulation results, this temperature difference closely follows the total heat produced by the reaction.

### Model

The total mass is constant, and it is assumed that the volume is constant as well. For the consecutive reactions the two component balances are

$$\frac{dC_A}{dt} = -k_1 C_A$$

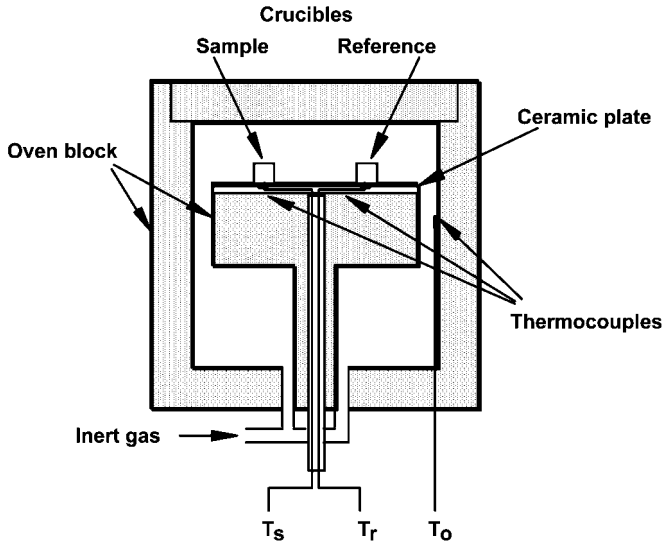


Fig. 1. Differential Scanning Calorimeter (DSC).  $T_s$ =sample temperature,  $T_r$ =reference temperature,  $T_o$ =oven temperature.

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

The rate constants  $k_1$  and  $k_2$  are functions of the temperature

$$k_1 = k_{01} \exp\left(-\frac{E_{a1}}{R T_s}\right)$$

$$k_2 = k_{02} \exp\left(-\frac{E_{a2}}{R T_s}\right)$$

The heat production rates are given by

$$q_1 = -k_1 C_A \Delta H_1$$

$$q_2 = -k_2 C_B \Delta H_2$$

The heat balance for the reference crucible is

$$\frac{dT_r}{dt} = \frac{UA(T_o - T_r)}{C_{pc}m_c}$$

The heat balance of the sample crucible yields

$$\frac{dT_r}{dt} = \frac{UA(T_o - T_s) + (q_1 + q_2)V_s}{c_{pc}m_c + c_{ps}m_s}$$

### Exercises

1. Vary the activation energies of the two reactions and note for which values the reaction can be distinguished from a single decomposition reaction. Compare these results by “turning off” the second reaction and enhancing the first by setting  $k_{02} = 0$  and setting  $\Delta H_1 = -500000$  J/mol.
2. Study the influence of the oven heating rate on the resolution of the two measured peaks.
3. Modify the program to study isothermal differential calorimetry by operating at constant temperature for a series of runs. Estimate the activation energy with Arrhenius plots from the rates observed at constant conversion.
4. Modify the program to study an auto-catalytic reaction ( $A \rightarrow B$  and  $A+B \rightarrow 2B$ ).
5. Modify the existing program to study adiabatic decomposition. Compare the results with those for an adiabatic decomposition of an auto-catalytic reaction.

### Nomenclature

#### Symbols

C	Concentration	mol/m <sup>3</sup>
$c_p$	Heat capacity	J/K kg
$E_a$	Activation energy	J/mol
k	Rate constants	1/s
$k_0$	Preexponential factors	1/s
m	Mass	kg
q	Heat production rate	J/m <sup>3</sup> s
r	Reaction rate	mol/m <sup>3</sup> s
T	Temperature	h
UA	Heat transfer coefficient	J/ K s
V	Volume	m <sup>3</sup>
$\Delta H$	Reaction enthalpy	J/ mol
$\rho$	Density	kg/m <sup>3</sup>
$\tau$	Measurement delay	1/s

#### Subscripts

A	Refers to reactant A
B	Refers to intermediate B
c	Refers to crucible
o	Refers to oven
r	Refers to reference
S	Refers to sample
1	Refers to the first reaction
2	Refers to the second reaction

## Results

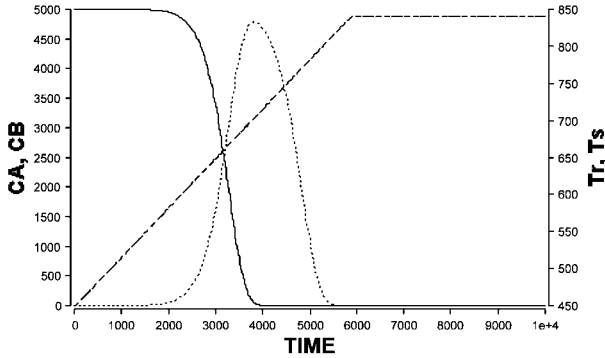


Fig. 2. Concentration and temperature profiles in a DSC measurement of a consecutive reaction.

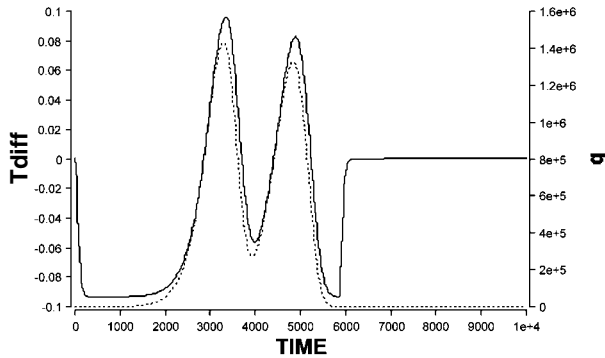


Fig. 3. Temperature difference between sample and reference crucibles (solid line) and the total heat production (dashed line).

## Reference

Keller, A., Stark, D., Fierz, H., Heinzle, E., Hungerbühler, K. (1997) Estimation of the time to maximum rate using dynamic DSC experiments. *J. Loss Prev. Process Ind.* 10, 31–41.

### 5.2.10

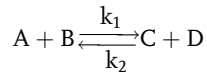
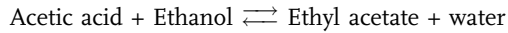
#### ESTERFIT – Esterification of Acetic Acid with Ethanol. Data Fitting

## System

In this example, the determination of rate constants by curve-fitting the model to real experimental data is demonstrated.

The process involves ethanol and acetic acid reacting reversibly to ethyl acetate, using a catalyst, ethyl hydrogen sulfate, which is prepared by reaction be-

tween sulfuric acid and ethanol. After equilibration of sulphuric acid with ethanol, acetic acid is added to the batch reactor in equimolar amounts, equivalent to the remaining free ethanol.



### Model

The rate of batch reaction for reactant A (acetic acid) is modelled as

$$\frac{dC_A}{dt} = r_A = -k_1 C_A C_B + k_2 C_C C_D$$

The progress of the reaction is followed by taking samples at regular time intervals and titrating the remaining free acid with alkali (mL).

### Program

The program is on the CD.

### Experimental Data

The file of experimental data (ESTERdat) giving time (min.) versus mL titrated is on the disk.

### Nomenclature

#### Symbols

C	Component concentration	kmol/m <sup>3</sup>
k	Second-order reaction rate constant	m <sup>3</sup> /kmol s
t	Time	min

#### Indices

- 1, 2, 3, 4    Refer to reactions  
 A, B, C, D    Refer to components

## Exercises

1. Study the effect of varying rate coefficients  $k_1$ ,  $k_2$  in the range (0.001 to 0.1) on the time-dependent concentrations of A, B, C and D. Starting from the default values (use RESET in the Parameter Menu) make one run each with a lower and higher  $k_1$  value. Repeat the same for  $k_2$ . Describe the effects of these changes. Use Overlay-Plots to document the changes.
2. Starting from the default values, decrease both  $k_1$  and  $k_2$  by half simultaneously. Then double both values starting from default. Describe the resulting effects. Again use overlay-plots.
3. Start again from default values. Modify the initial amount of water (CD\_init), using values about 2 and 4 times the default values.
4. Import the table of measured data, which actually originate from a student experiment, into the program from the external file ESTERdat.txt (Menu Model/Datasets). Data are listed as time (min) versus titrated volume (mL). Modify the plot window correspondingly (Double click. Now, adjust Integration Time, STOPTIME, to see all data points. Modify  $k_1$  and  $k_2$  manually to obtain an optimal fit of measured data (MLtitrated) to experimental data (#ESTERdat).
5. Use the Curve Fit tool to obtain optimal results automatically. Document the differences to the manually obtained results. Clicking CURVE-FIT will allow the selection of the variable to be fit to the experimental data and the parameters to be determined. For each parameter, two initial guessed values and the maximum and minimum allowable values can be entered. Limit  $k_1$  and  $k_2$  to positive values. On running under CURVE-FIT, the values of the required parameters are repeatedly updated until the final converged values are obtained. The updated values can be found in the Parameter Window.

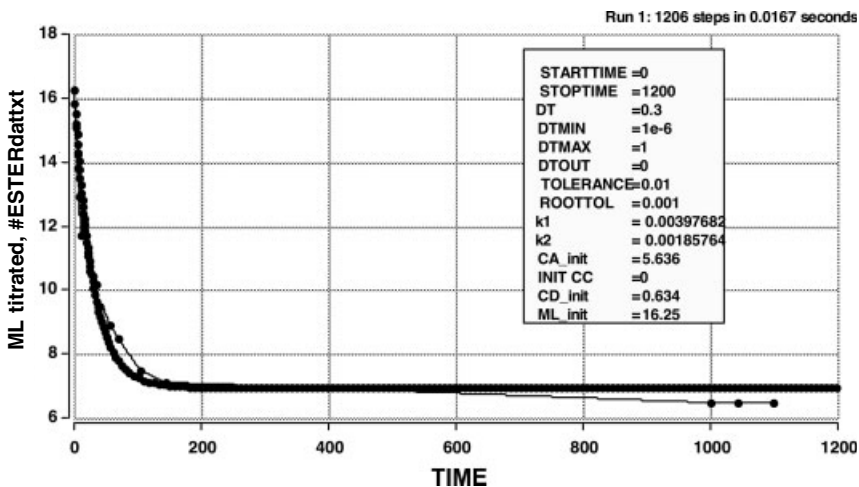


Fig. 1. Results of the Curve Fit. The simulation is the bold curve.

6. One student wanted to get a quick result. Instead of including the values obtained at equilibrium, he/she just used the values until 180 min for parameter estimation. Compare the results with those of exercise 5 and comment.
7. It is assumed that the initial titration to yield  $ML_{init}$  is quite erroneous. Therefore,  $ML_{init}$  is also adjusted to improve the fit. What are the changes resulting?

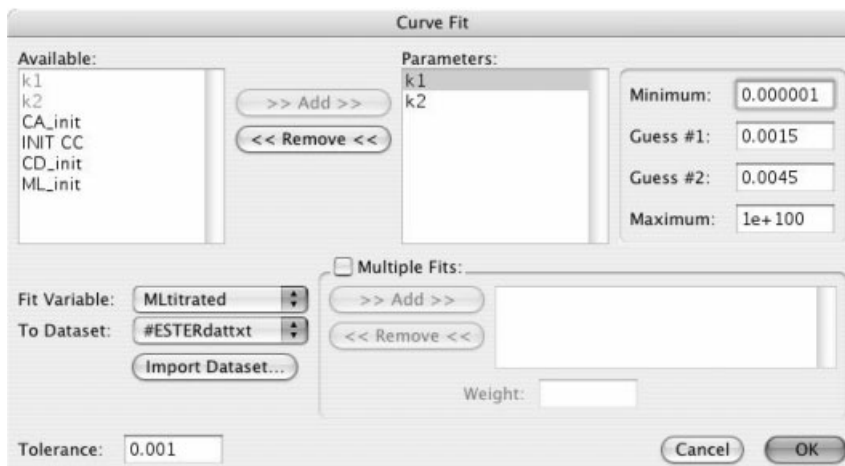


Fig. 2. Set-up of the Curve Fit window.

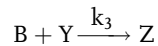
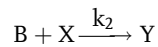
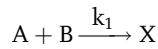


### 5.3 Continuous Tank Reactor Examples

#### 5.3.1 CSTRCOM – Isothermal Reactor with Complex Reaction

##### System

Complex reactions can be conveniently investigated by simulation techniques. In this example from Russell and Denn (1972), the characteristics of the following complex reaction can be investigated.



This sequential-parallel reaction has sequential ( $A \rightarrow X \rightarrow Y \rightarrow Z$ ) as well as parallel characteristics ( $B \rightarrow X$ ,  $B \rightarrow Y$ ,  $B \rightarrow Z$ ).

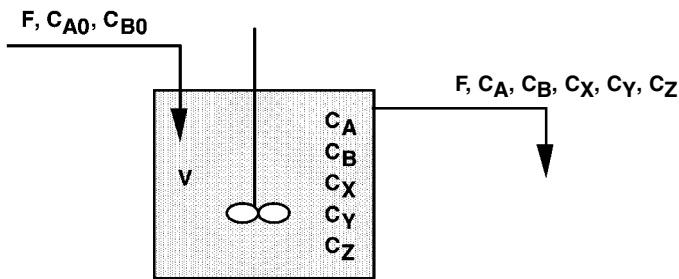


Fig. 1 Stirred tank with series-parallel reaction.

##### Model

For each component

$$\left( \begin{array}{c} \text{Rate of} \\ \text{accumulation} \\ \text{in reactor} \end{array} \right) = \left( \begin{array}{c} \text{Rate of} \\ \text{flow} \\ \text{in} \end{array} \right) - \left( \begin{array}{c} \text{Rate of} \\ \text{flow} \\ \text{out} \end{array} \right) + \left( \begin{array}{c} \text{Rate of} \\ \text{formation} \\ \text{by reactor} \end{array} \right)$$

All three reactions are assumed to follow simple second-order kinetics, and thus the mass balances become

$$V \frac{dC_A}{dt} = F(C_{A0} - C_A) - V k_1 C_A C_B$$

$$V \frac{dC_B}{dt} = F(C_{B0} - C_B) - V k_1 C_A C_B - V k_2 C_B C_X - V k_3 C_B C_Y$$

$$V \frac{dC_X}{dt} = F(C_{X0} - C_X) + V k_1 C_A C_B - V k_2 C_B C_X$$

$$V \frac{dC_Y}{dt} = F(C_{Y0} - C_Y) + V k_2 C_B C_X - V k_3 C_B C_Y$$

$$V \frac{dC_Z}{dt} = F(C_{Z0} - C_Z) + V k_3 C_B C_Y$$

Dividing by  $V$ , the equations can be written in terms of the mean residence time of the reactor,  $\tau = F/V$ .

## Nomenclature

### Symbols

C	Concentration	kmol/m <sup>3</sup>
F	Flow rate	m <sup>3</sup> /s
k	Rate constant	m <sup>3</sup> /kmol s
V	Volume	m <sup>3</sup>

### Indices

A, B, X, Y, Z	Refer to components
1, 2, 3	Refer to the reaction steps

### Exercises

1. Compare the steady-state values of A, B, X, Y, Z with calculated values obtained by solving the steady-state component balance equations for this problem.
2. Study the effect of varying residence time  $\tau$  (by changing feed rate), feed concentration, and rate constants on reactor performance. This can be done using "Parametric Runs" to obtain plots of the steady state concentrations as final values versus the corresponding change in parameter.
3. Note that when  $k_1 = k_2 = k_3 = 0$ ,  $C_{A0} = 1$ ,  $C_{B0} = 0$ , the program solves the case of a step input of tracer solution, which can be used to generate the typical F-diagram for a single perfectly mixed tank. Compare this result with the analytical solution.

## Results

The concentration levels are very sensitive to the kinetic parameters. Using the parameters in the program the following results were obtained

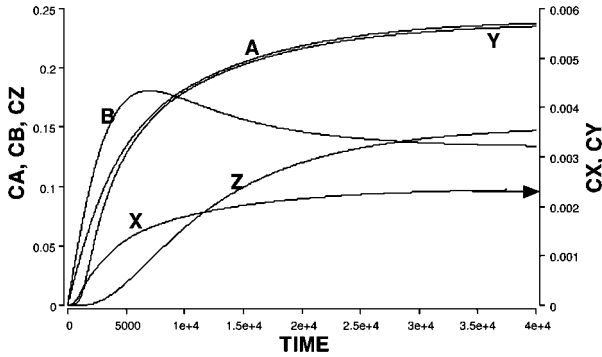


Fig. 2 Start up of the reactor for the  $F = 0.0001$ , i.e. residence time  $\tau = 10000$  s. The components X and Y are present at very small concentrations (right hand scale).

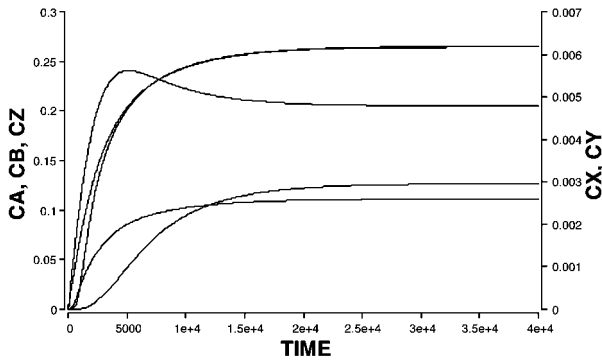


Fig. 3 Start up of the reactor for the  $F = 0.0002$ , i.e. residence time  $\tau = 5000$  s. The components X and Y are present at very small concentrations (right hand scale).

## Reference

Russell, T.W.F. and Denn, M.M. (1972) Introduction to Chemical Engineering Analysis, McGraw-Hill.

## 5.3.2

**DEACT – Deactivating Catalyst in a CSTR****System**

Solid catalysts can be conveniently studied in loop reactors, which allow measuring the reaction rates by concentration difference measurement across the catalyst bed. When operated continuously with high recycle rate, the entire loop usually can be modelled as a single well-stirred tank. Here the case of catalyst deactivation is studied.

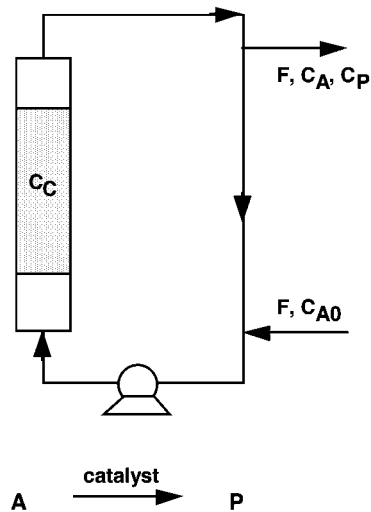


Fig. 1 A continuous recycle-loop reactor for catalyst studies.

**Model**

The model mass balances are formulated in mol quantities. The kinetics are assumed to be

$$r_A = -\frac{kC_C C_A}{1 + K_A C_A}$$

and

$$r_P = -r_A$$

The mass balance for component A for the entire loop is

$$\frac{dC_A}{dt} = \frac{C_{A0} - C_A}{\tau} = r_P$$

where  $\tau$  is calculated as the volume of the entire loop system divided by the entering flow rate,  $V/F$ .

The mass balance for product P is

$$\frac{dC_P}{dt} = -\frac{C_P}{\tau} + r_P$$

The batch balance for the catalyst with first-order deactivation is

$$\frac{dC_C}{dt} = -k_D C_C$$

## Nomenclature

### Symbols

C	Concentration	mol/m <sup>3</sup>
C <sub>C</sub>	Catalyst concentration	kg/m <sup>3</sup>
F	Flow rate	m <sup>3</sup> /h
k	Reaction rate constant	m <sup>3</sup> /kg h
K <sub>A</sub>	Kinetic constant	m <sup>3</sup> /mol
K <sub>D</sub>	Deactivation constant	1/h
r	Reaction rate	mol/m <sup>3</sup> h
$\tau$	Residence time in loop	h
V	Total loop reactor volume	m <sup>3</sup>

### Indices

A, C, P	Refer to reactant, catalyst and product
0	Refers to initial value

### Exercises

1. Observe the influence of the catalyst decay constant,  $K_D$ , on the outlet product concentration. Make runs for a range of  $K_D$  values.
2. Design and carry out simulated experiments to evaluate the proposed reaction kinetics expression.
3. Assuming P can be measured, devise and program a control system to keep the product level constant.

## Results

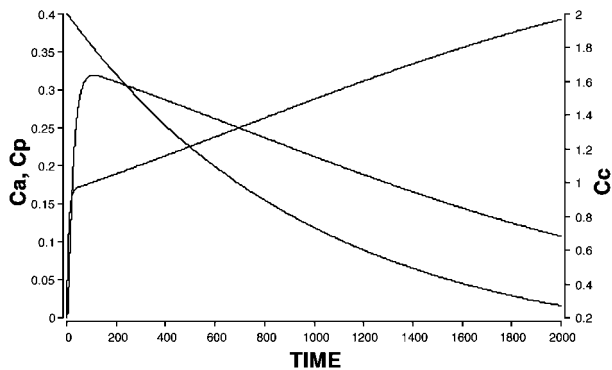


Fig. 2 Long time effect of the catalyst deactivation,  $C_c$ , on the concentrations  $C_a$  and  $C_p$ .

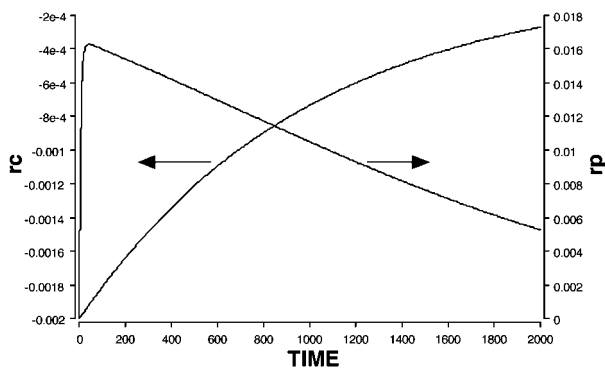


Fig. 3 The influence of  $rc$  changes on the production rate,  $rp$ .

### 5.3.3

#### TANK and TANKDIM – Single Tank with Nth-Order Reaction

##### System

An  $n$ th-order reaction is run in a continuous stirred-tank reactor. The model and program are written in both dimensional and dimensionless forms. This example provides experience in the use of dimensionless equations.

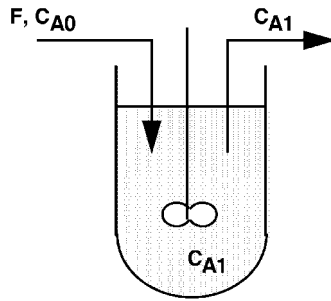


Fig. 1 A continuous tank reactor with  $n$ th-order reaction.

### Model

The balance for the reactant A is

$$V \frac{dC_{A1}}{dt} = F(C_{A0} - C_{A1}) + r_A V$$

and the kinetics are

$$r_A = -k C^{n,A1}$$

Dimensionless variables are defined as

$$\bar{C}_{A1} = \frac{C_{A1}}{C_{A0}}, \quad \bar{C}_{A0} = \frac{C_{A0}}{C_{A0}} = 1 \quad \text{and} \quad \bar{t} = \frac{t}{\tau}$$

where  $\tau$ , the residence time, is  $V/F$ .

The dimensionless balance equation is then

$$\frac{d\bar{C}_{A1}}{d\bar{t}} = (1 - \bar{C}_{A1}) + \frac{\tau}{C_{A0}} r_A$$

and the rate equation becomes

$$\bar{r}_A = -k C_{A0}^n \bar{C}_{A1}^n$$

Thus the governing dimensionless parameter is  $[k \tau C_{A0}^{n-1}]$ .

### Program

Program TANK solves the normal dimensional model equation for the problem, whereas TANKDIM is formulated in terms of the dimensionless model equations.

## Nomenclature

### Symbols

$C_{A0}$	Feed concentration	$\text{kg}/\text{m}^3$
$C_{A1}$	Concentration in reactor	$\text{kg}/\text{m}^3$
$F$	Feed	$\text{m}^3/\text{s}$
$k$	Reaction constant	$\text{m}^{3(n-1)}/\text{kg}^{n-1}\text{s}$
$n$	Reaction order	–
$\tau$	Residence time	s
$t$	Time	s
$V$	Volume	$\text{m}^3$

### Exercises

Starting with program TANK:

1. Run the simulation for a range of residence times. When are the steady states reached?
2. Change the initial concentration and rerun the simulations.
3. Turn off the flow by setting the value of TAU initially very high, and start the reactor as a batch system. Change over to continuous operation using the IF-THEN-ELSE statement to define a value of TAU.
4. Run for several values of  $n$  and plot  $r_A$  versus  $C_{A1}$  for each case. Calculate the steady-state concentrations for  $n = 0$ ,  $n = 1$  and  $n = 2$ .
5. Compare the results from TANK and TANKDIM for a range of parameters.
6. Calculate the steady state for  $n = 1$  by hand. Run the simulation and compare. Change  $C_{A0}$  for this case and run. Compare the effects on  $\bar{C}_{A1}$  and  $C_{A1}$ .
7. Investigate the time to reach steady state for various parametric values.
8. With zero initial conditions, run for  $n = 0$ ,  $n = 1$ ,  $n = 1.5$  and  $n = 2$ . Plot  $r_A$  versus  $C_{A1}$  and compare.

### Results

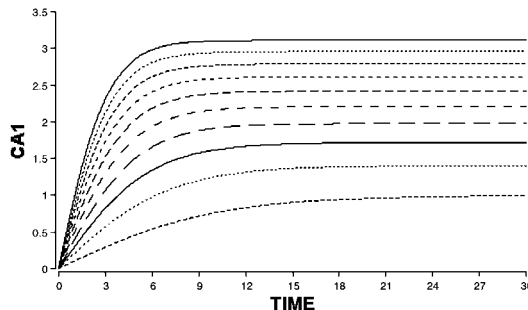


Fig. 2 Startup for a range of flow rates using the program TANK.



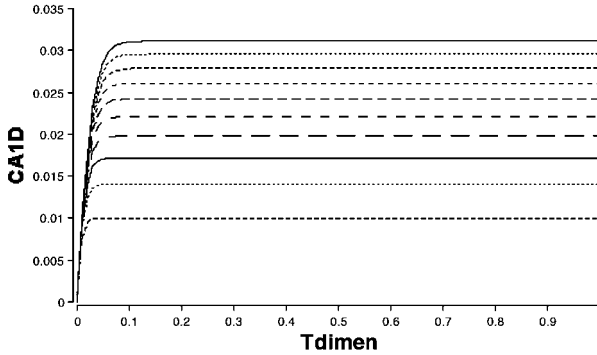


Fig. 3 Dimensionless results from TANKDIM corresponding to the same flow rates as the run in Fig. 2.

#### 5.3.4

#### CSTRPULSE – Continuous Stirred-Tank Cascade Tracer Experiment

##### System

A system of  $N$  continuous stirred-tank reactors is used to carry out a first-order isothermal reaction. A simulated pulse tracer experiment can be made on the reactor system, and the results can be used to evaluate the steady state conversion from the residence time distribution function (E-curve). A comparison can be made between reactor performance and that calculated from the simulated tracer data.

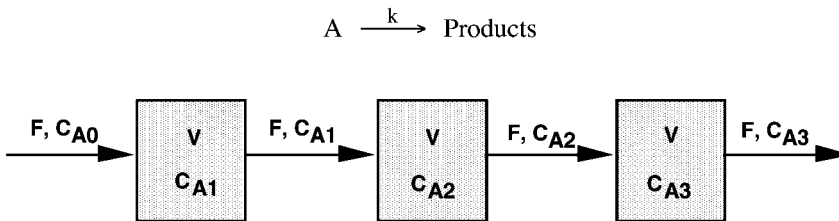


Fig. 1 Tanks-in-series with first-order reaction.

##### Model

Component balances for the three tanks give

$$\text{Tank 1} \quad V \frac{d(C_{A1})}{dt} = F(C_{A0} - C_{A1}) - V k C_{A1}$$

$$\text{Tank 2} \quad V \frac{d(C_{A2})}{dt} = F(C_{A1} - C_{A2}) - V k C_{A2}$$

$$\text{Tank 3} \quad V \frac{d(C_{A3})}{dt} = F(C_{A2} - C_{A3}) - V k C_{A3}$$

or dividing by V

$$\frac{d(C_{A1})}{dt} = \frac{C_{A0} - C_{A1}}{\tau_1} - k C_{A1}$$

$$\frac{d(C_{A2})}{dt} = \frac{C_{A1} - C_{A2}}{\tau_2} - k C_{A2}$$

$$\frac{d(C_{A3})}{dt} = \frac{C_{A2} - C_{A3}}{\tau_3} - k C_{A3}$$

where the mean residence time  $\tau$  in tank n is given by

$$\tau_n = \frac{V_n}{F}$$

Thus for tank n the balances have the form

$$\frac{dC_{An}}{dt} = \frac{C_{An-1} - C_{An}}{\tau_n} - k C_{An}$$

where for the tracer experiments, the reaction rate term is, of course, set to zero.

Information from tracer experiments can be used to calculate the steady state conversion according to the following relationship (Levenspiel, 1999)

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

The E-curve is evaluated by measuring experimentally the outlet tracer concentration versus time curve from a tracer pulse input and applying the following defining equation

$$E(t) = \frac{C}{\int C dt}$$

### Program

The program is formulated in vector form, allowing for any number of tanks N in the cascade but with all N tanks having an equal volume, V. The function PULSE is used in the program in relation to the tracer experiments, and the calculation of the actual conversion based on the E curve data is made by the program. Instructions on its use are found within the program.

**Nomenclature****Symbols**

$C_{An}$	Concentration of A in tank n	$\text{kmol/m}^3$
$C_{tr}$	Concentration of tracer leaving system	$\text{kmol/m}^3$
$F$	Flow rate	$\text{m}^3/\text{s}$
$k$	Rate constant	$1/\text{s}$
$V$	Volume of all tanks	$\text{m}^3$
$\tau_n$ and $\text{Tau}$	Residence time in each tank	$\text{s}$
$E$	E-curve	$1/\text{s}$

**Indices**

0, 1, 2, 3, n Refer to tank number

**Exercises**

1. Study the effect of varying the total volume  $V$ , the number of tanks, and the rate constant on the performance of the reaction cascade.
2. Compare the steady state concentration values obtained with those from the solution of the steady state balance equations.
3. Setting  $k = 0$ , simulate the response to a pulse of tracer for 3 perfectly-stirred tanks in series. Repeat this for various numbers of tanks and plot  $E$  versus dimensionless time for these on an overlay graph.
4. Use the  $E$ -curve from a simulated tracer experiment to calculate the conversion for 3 tanks. Compare this result with that obtained by a simulation with reaction.
5. Compare the steady-state values obtained with the solution of the steady-state algebraic equations.
6. Derive the dimensionless form of the balances to show  $k\tau$  to be the governing parameter. Run simulations to confirm this.
7. Change the program to compare the conversion from various combinations of tank volumes such that the total volume is constant. For a total volume of 10 L this could be a tank of 2.5 L followed by 2.5 L and 5 L, or this sequence could be reversed.

## Results

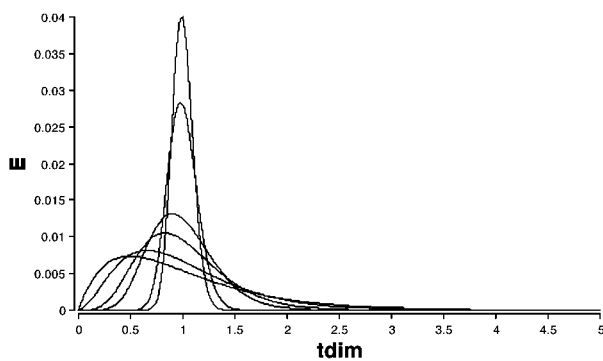


Fig. 2 Residence time distribution curves for  $N = 2, 3, 6, 10, 50$  and  $100$ .

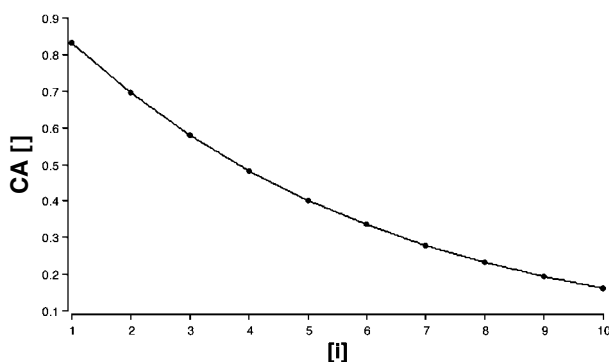


Fig. 3 Concentrations in 10 tanks with reaction at steady state.

## Reference

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

### 5.3.5

#### CASCSEQ – Cascade of Three Reactors with Sequential Reactions

#### System

A cascade of 3 tanks in series is used to optimise the selectivity of a complex sequential-parallel reaction. Depending on the kinetics, distributing the feed of one reactant among the tanks may lead to improved selectivity.

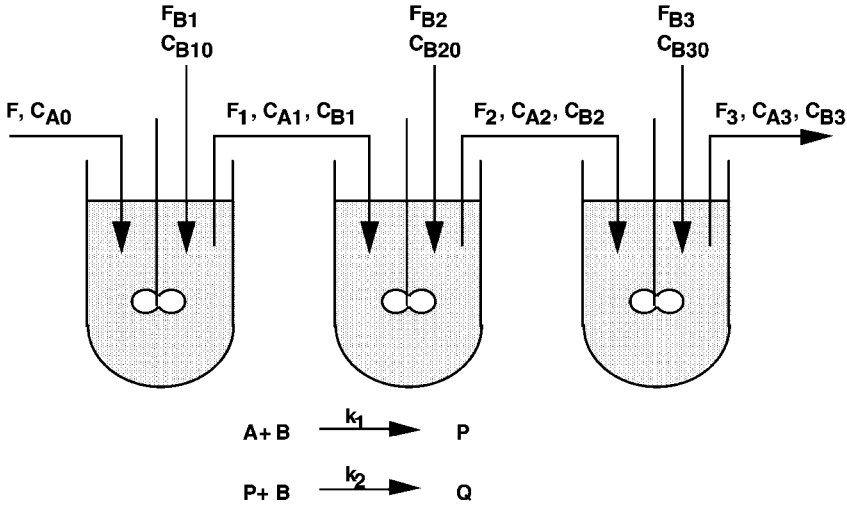


Fig. 1 Stirred tanks in series with feeding to accomplish the best performance with this complex reaction.

### Model

The kinetics are

$$r_A = -k_1 C_A^{n_A} C_B^{n_{B1},B}$$

$$r_B = -k_1 C_A^{n_A} C_B^{n_{B1},B} - k_2 C_P^{n_P} C_B^{n_{B2},B}$$

$$r_P = -k_1 C_A^{n_A} C_B^{n_{B1},B} - k_2 C_P^{n_P} C_B^{n_{B2},B}$$

$$r_Q = +k_2 C_P^{n_P} C_B^{n_{B2},B}$$

The component balances for tank 2 are

$$\frac{VdC_{A2}}{dt} = F_1 C_{A1} - F_2 C_{A2} + r_A V$$

$$\frac{VdC_{B2}}{dt} = F_1 C_{B1} - F_2 C_{B2} + r_B V$$

$$\frac{VdC_{P2}}{dt} = F_1 C_{P1} - F_2 C_{P2} + r_P V$$

$$\frac{VdC_{Q2}}{dt} = F_1 C_{Q1} - F_2 C_{Q2} + r_Q V$$

The other tanks have analogous balances.

Note that the flow rates vary from tank to tank

$$F_1 = F + F_{B1}$$

$$F_2 = F + F_{B1} + F_{B2}$$

$$F_3 = F + F_{B1} + F_{B2} + F_{B3}$$

## Nomenclature

### Symbols

$V_1, V_2, V_3$	Initial tank volume	$m^3$
$C_{A0}$	Concentration of A in feed	$kmol/m^3$
$C_{B10}$	Concentration of B in feed to tank 1	$kmol/m^3$
$C_{B20}$	Concentration of B in feed to tank 2	$kmol/m^3$
$C_{B30}$	Concentration of B in feed to tank 3	$kmol/m^3$
$F$	Flow rates	$m^3/s$
$k_1$	Rate constant reaction 1	depends on n
$k_2$	Rate constant reaction 2	depends on n
$n$	Reaction order	–

### Subscripts

A,B,C,P,Q	Refer to components
1,2,3	Refer to tanks
0	Refers to inlet
Init	Refers to initial

### Exercises

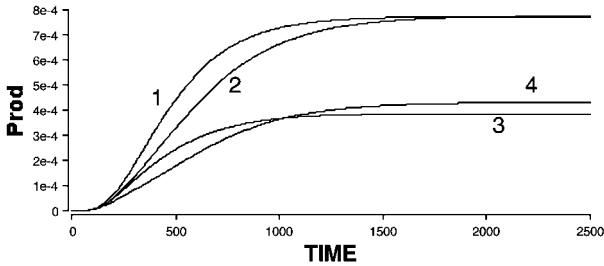
1. Set  $n_{B1} = n_{B2}$ , and set equal feed concentrations of B and A to tank 1. Keeping  $F = F_{B1}$ , vary the volumetric flows to the reactor cascade and study the effect of total holdup time on the maximum concentration of the product  $C_{P3}$ .
2. Feed B at differing rates into each tank, but maintain the same total molar flow rate of B, as in Exercise 1. Carry out simulations for the kinetic case  $n_{B1} < n_{B2}$  and optimise the resultant selectivity. Show by simulation that high values for  $C_{P3}$  are given by low values of  $C_B$ .
3. Repeat Exercises 1, 2 for the kinetic case  $n_{B1} > n_{B2}$ . Now high  $C_{P3}$  will be obtained with high  $C_B$ . Explain the results obtained with reference to Section 3.2.11.
4. By varying  $k_2$  relative to  $k_1$ , investigate the influence of the kinetic constant ratio on the selectivity.

## Program

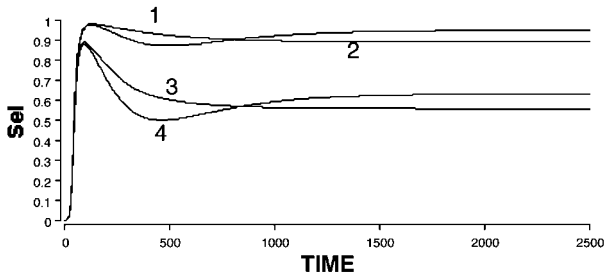
The program calculates some quantities, such as selectivity, that are valid only at the steady state condition.

## Results

Startup and steady states are shown for the kinetic case  $k_1 = 0.1$ ,  $k_2 = 0.05$ ,  $n_A = 1$ ,  $n_P = 1$ ,  $n_{B1} = 1$  and  $n_{B2} = 1$  or  $2$ .



**Fig. 2** When all of reactant B was fed into tank 1 with flow rate  $F_{B1} = 0.003$  (curves 1, 3). The productivity was slightly lower than in the case for equal distribution of reactant B to all tanks (2, 4). Higher reaction order with respect to B gave higher productivity ( $n_{B2} = 2$ : curves 1, 2). The maximum productivity possible was 0.001.



**Fig. 3** Distributing reactant B with feed rates  $F_{B1} = F_{B2} = F_{B3} = 0.001$  (curves 2, 4) gave lower concentrations of B in all tanks and consequently a higher selectivity. The productivity was also slightly higher (0.13 compared to 0.12). A higher reaction order with respect to B gave high selectivity ( $n_{B2} = 2$ : curves 1, 2).

## 5.3.6

## REXT – Reaction with Integrated Extraction of Inhibitory Product

## System

Consider the necessity to extract a product, which impedes a reaction in a continuous tank system. This can be accomplished with an integrated extraction unit, here a liquid–liquid extraction system.

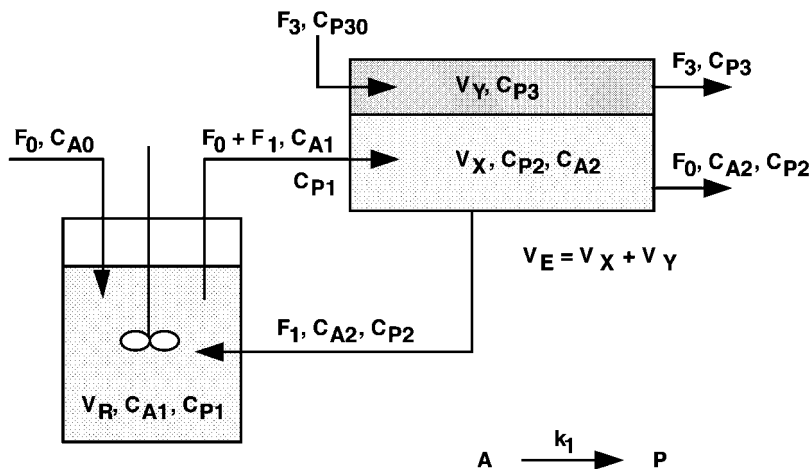


Fig. 1 Integrated reaction and liquidliquid extraction.

## Model

The kinetics exhibit inhibition by the product,

$$-r_A = r_P = \frac{k_1 C_{A1}}{1 + \frac{C_{P1}}{K_i}}$$

The balances for reactant and product in the reactor are for A

$$V_R \frac{dC_{A1}}{dt} = F_0 C_{A0} + F_1 C_{A2} - (F_0 + F_1) C_{A1} - V_R r_P$$

and for P

$$V_R \frac{dC_{P1}}{dt} = F_1 C_{P2} - (F_0 + F_1) C_{P1} + V_R r_P$$

The single-stage extraction unit is modelled by balances for P in both phases X and Y as follows:



$$\frac{d(V_X C_{P2})}{dt} = (F_0 + F_1)C_{P1} - F_1 C_{P2} - F_0 C_{P2} - K_a V_E (C_{P3}^* C_{P3})$$

$$\frac{d(V_Y C_{P3})}{dt} = F_3 C_{P30} - F_3 C_{P3} + K_a V_E (C_{P3}^* - C_{P3})$$

where the equilibrium is given by

$$C_{P3}^* = m C_{P2}$$

The reactant is not removed by the extraction. Thus,

$$\frac{d(V_X C_{A2})}{dt} = (F_0 + F_1)C_{A1} - F_0 C_{A2} - F_1 C_{A2}$$

The recycle flow,  $F_1$ , can be written in terms of fraction recycled  $R$  as

$$F_1 = R F_0$$

Thus,

$$F_0 + F_1 = (1 + R)F_0$$

### Program

The program also calculates the production rate of the extractor and the conversion fraction, product produced/reactant fed.

### Nomenclature

#### Symbols

$F_0$	Feed rate of A	$m^3/s$
$C$	Concentration	$kmol/m^3$
$F_3$	Extraction solvent flow	$m^3/s$
$C_{P3}$	Product concentration in solvent	$kmol/m^3$
$R$	Recycle ratio	—
$V_R$	Reactor volume	$m^3$
$V_Y$	Solvent volume	$m^3$
$V_X$	Extract volume of solvent	$m^3$
$k_1$	Reaction constant	$1/s$
$K_I$	Inhibition constant	$kmol/m^3$
$m$	Saturation constant	—
$K_a$	Specific transfer coefficient	$1/s$
$V_E$	Total extractor volume	$m^3$

### Indices

A, P	Refer to reactant and product
0, 1, 2, 3	Refer to steams
X, Y	Refer to extractor phases

### Exercises

1. Verify that the component balances for the system are correct at steady state.
2. Vary the main operating variables for the reactor system and note their influence on the conversion efficiency for differing values of the inhibition coefficient,  $K_I$ .
3. Study the effect of the extraction stage on reactor performance by varying the magnitudes of the the mass transfer coefficient  $K_a$ , the equilibrium distribution ratio  $m$ , the recycle ratio  $R$ , the relative reactor and extraction volumes and solvent flowrate.
4. The introduction of a solvent extraction process and an increasing flow of solvent in order to improve extraction efficiency constitute an increased environmental loading on the system. How might one take account of such effects in the simulation program?

### Results

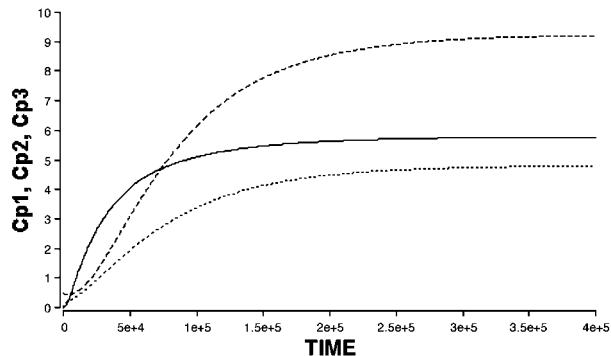


Fig. 2 Startup with recycle ratio  $R = 0.5$  showing the product concentrations reaching steady-state.

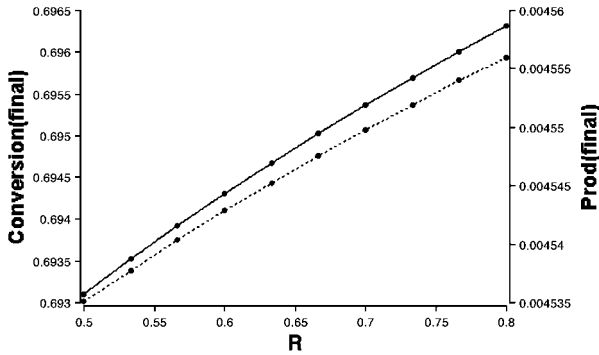


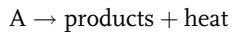
Fig. 3 Steady-state fraction conversion and productivity of the process as a function of recycle ratio.

### 5.3.7

#### THERM and THERMPLOT – Thermal Stability of a CSTR

##### System

A first-order, exothermic reaction occurs within a continuous stirred-tank reactor, equipped with jacket cooling, where the kinetics and reactor schemes are



$$-r_A = kC_A \quad k = Ze^{-E/RT_R}$$

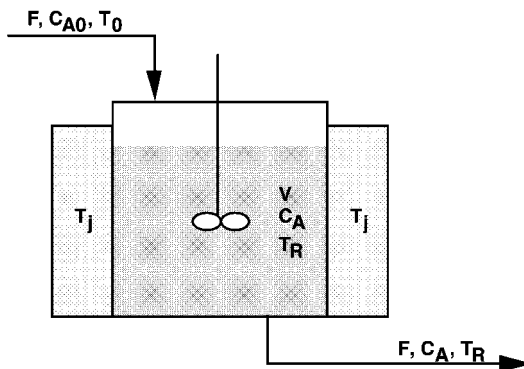


Fig. 1 Continuous tank with heat transfer to jacket.

**Model**

The dynamic model involves a component mass balance, an energy balance, the kinetics and the Arrhenius relationship. Hence

$$V \frac{dC_A}{dt} = F C_{A0} - F C_A - k V C_A$$

$$V \rho c_p \frac{dT_R}{dt} = F \rho c_p (T_0 - T_R) - k V C_A (-\Delta H) - UA(T_R - T_j)$$

The steady-state equations allow evaluation of the possible steady-state operating points. For the component balance:

$$F C_{A0} = F C_A + k V C_A$$

Giving

$$C_A = \frac{C_{A0}}{1 + (kV/F)}$$

Separating the energy balance into heat loss and heat generation terms:

$$\text{Rate of heat loss (H}_L\text{)} = \text{Rate of heat generation (H}_G\text{)}$$

$$F \rho c_p (T_R - T_0) + UA(T_R - T_j) = -k V C_A (-\Delta H)$$

which with the mass balance gives

$$F c_p (T_R - T_0) + UA(T_R - T_j) = k V C_{A0} \Delta H / (1 + (kV/F))$$

**Programs**

Program **THERMPLOT** models the steady-state variation in  $H_L$  and  $H_G$  as a function of temperature. For the conditions of this reaction, there may be three possible steady-state operating conditions for which  $H_G = H_L$ . Only two of these points, however, are stable.

Program **THERM** solves the dynamic model equations. The initial values of concentration and temperature in the change with in multiple runs with Madonna or with sliders Note that for comparison, both programs should be used with the same parameter values.

Portions of the programs are shown below.

```
{Example THERMPLOT}
{TEMP IS CHANGED BY DUMMY INTEGRATION}
INIT TR=250
d/dt (TR)=1 {TR becomes TR+250}
```

```

K0=Z*EXP(-E/(R*273))
K=K0*EXP(-(E/R)*(1/TR-1/273)) {AVOIDS MATH OVERFLOW}
CA=CA0/(1+K*V/F) {STEADY STATE MASS BALANCE}
HL = F*(TR-T0)/V+UA*(TR-TJ)/(V*RHO*CP) {HEAT LOSS}
HG = -K*CA*HR/(CP*RHO) {HEAT GAIN}

```

{Example THERM}

```

K0=Z*EXP(-E/(R*273)) {Rate constant at 273 K, 1/s}
K=K0*EXP(-(E/R)*(1/TR-1/273)) {Avoidsmath overflow}

```

{Dynamic mass balance, first order kinetics}

```
d/dt(CA) = F*(CA0-CA)/V-K*CA
```

```
Limit CA>=0
```

{Dynamic energy balance}

{Heat lost, K/s}

```
HL = F*(TR-T0)/V+UA*(TR-TJ)/(V*RHO*CP)
```

```
HG = -K*CA*HR/(CP*RHO) {Heat gained, K/s}
```

```
d/dt(TR) = HG-HL {Heat balance, K/s}
```

## Nomenclature

### Symbols

$c_p$	Specific heat	$\text{kJ/kg K}$
$\rho$	Density	$\text{kg/m}^3$
$F$	Volumetric feed rate	$\text{m}^3/\text{s}$
$V$	Reactor volume	$\text{m}^3$
$UA$	Heat transfer capacity coefficient	$\text{kJ/K s}$
$\Delta H$	Exothermic heat of reaction	$\text{kJ/kmol}$
$T$	Feed temperature	$\text{K}$
$T_R$	Reactor temperature	$\text{K}$
$C$	Concentration	$\text{kmol/m}^3$
$Z$	Collision frequency	$1/\text{s}$
$E$	Activation energy	$\text{kJ/kmol}$
$R$	Gas constant	$\text{kJ/kmol K}$

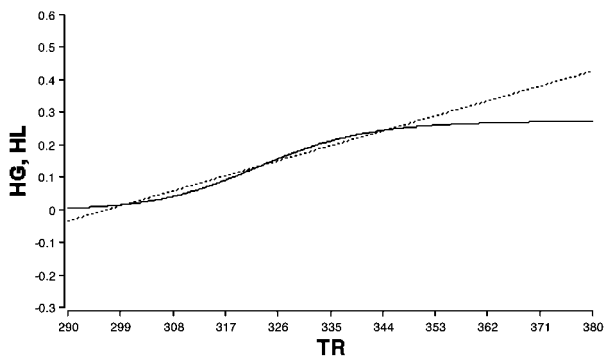
### Indices

0	Refers to feed condition
A	Refers to reactant
J	Refers to jacket

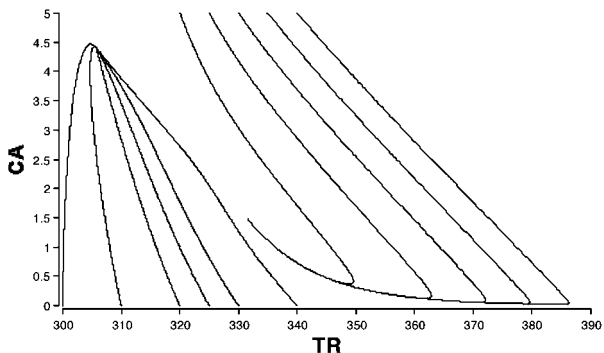
### Exercises

1. Using THERMPLOT, locate the steady states. With the same parameters, verify the steady states using THERM. To do this, change the initial conditions CAI and TRI using multiple runs or sliders. Plot as a phase-plane and also as concentration and temperature versus time.
2. Make small changes in the operating and design values ( $V$ ,  $F$ ,  $CA_0$ ,  $T_0$ ,  $T_j$ ,  $UA$ ) separately and note the effect on the steady states, using THERMPLOT. Verify each with THERM.
3. Choose a multiple steady-state case and try to upset the reactor by changing  $CA_0$ ,  $F$ ,  $T_0$  or  $T_j$ . Only very small changes are required to cause the reactor to move to the other steady state. Plot as time and phase-plane graphs.

### Results



**Fig. 2** Program THERMPLOT provides the graphical steady-state solution. The parameters in the program give two steady states and one unstable state.



**Fig. 3** This plot was made with THERM by changing the initial conditions TRI and CAI in two multiple runs on an overlay plot.

## Reference

Bilous, O., and Amundson, N. R. (1956) Chem. Eng. Sci., 5, 81.

### 5.3.8

#### COOL – Three-Stage Reactor Cascade with Countercurrent Cooling

##### System

A cascade of three continuous stirred-tank reactors arranged in series, is used to carry out an exothermic, first-order chemical reaction. The reactors are jacketed for cooling water, and the flow of water through the cooling jackets is countercurrent to that of the reaction (Fig.1).

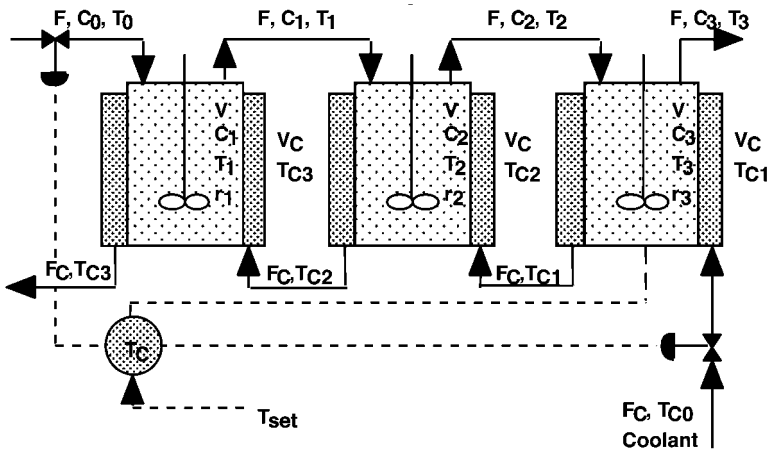


Fig. 1 A three-stage reactor system with countercurrent controlled cooling.

A variety of control schemes can be employed and are of great importance, since the reactor scheme shows a multiplicity of possible stable operating points. Obviously the aim in operating the reactor cascade is to ensure operation at the most favourable conditions, and for this both the startup policy and the control strategy are important. This example is taken from the paper of Mukesh and Rao (1977).

**Model**

The kinetics are

$$r_i = k_i C_i$$

where

$$k_i = Z^{-E/Rt_i}$$

The mass and heat balances in any reactor  $i$  are

$$V \frac{dC_i}{dt} = F(C_{i-1} - C_i) - V k_i C_i$$

$$\rho c_p V \frac{dT_i}{dt} = F \rho c_p (T_{i-1} - T_i) - V k_i C_i (-\Delta H) - UA(T_i - T_{ci})$$

For the cooling jackets of any reactor  $i$  the energy balance is

$$\rho_c c_{pc} V_C \frac{dT_{ci}}{dt} = F_C \rho_c c_{pc} (T_{ci-1} - T_{ci}) + UA(T_i - T_{ci})$$

**Nomenclature****Symbols**

$A$	Heat transfer area	$m^2$
$C_0$	Inlet concentration of A	$kmol/m^3$
$c_p$	Specific heat	$kJ/kg\ K$
$c_{pc}$	Coolant specific heat	$kJ/kg\ K$
$E$	Activation energy	$kJ/kmol$
$F$	Volumetric flow rate to reactor	$m^3/s$
$F_C$	Coolant flow	$m^3/s$
$R$	Gas constant	$kJ/kmol\ K$
$\rho$	Density	$kg/m^3$
$\rho_c$	Coolant density	$kg/m^3$
$T_0$	Inlet temperature	$K$
$T_{co}$	Coolant inlet temperature	$K$
$U$	Heat transfer coefficient	$kJ/m^2\ s\ K$
$V$	Reactor volume	$m^3$
$V_C$	Jacket volume	$m^3$
$Z$	Frequency factor	$1/s$
$\Delta H$ and $H_r$	Heat of reaction	$kJ/kmol$



### Exercises

1. Study the normal start up procedure with the reactors empty of reactant and cold ( $CA_1 = CA_2 = CA_3 = 0$ ,  $T_1 = T_2 = T_3 = 0$ ) and confirm that the system proceeds to a low yield condition.
2. By modifying the initial concentration and/or temperature profile along the cascade show that other stable operating conditions are realisable. This can be done by making a parametric runs to see how changes in any one parameter influence the steady state.
3. Investigate alternative start up policies to force the cascade to a more favourable, stable yield condition, as given below.
- 3a. Introduction of a feed-preheater and the effect of a short-burst preheat condition can be studied by starting with an increased value of the feed temperature,  $T_0$ , which is returned to normal once the reaction is underway. For this purpose a conditional operator is built into the program. Both the duration and temperature of the preheat can be defined.
- 3b. Temperature control of feed flow rate can be described by

$$F = F_0 - KC * (TSET - T_3)$$

Proportional control can be based on the temperature of the third stage. Here  $F_0$  is the base flow rate,  $KC$  is the proportional controller gain, and  $TSET$  is the temperature set point. Note that in order to guard against the unrealistic condition of negative flow, a limiter condition on  $F$  should be inserted. This can be accomplished with MADONNA by the following statement

$$\text{LIMIT } F \geq 0$$

- 3c. Temperature control of coolant flow can be described by

$$FC = FC_0 - KC * (TSET - T_3)$$

A limiter on  $FC$  should be used as in 3b.

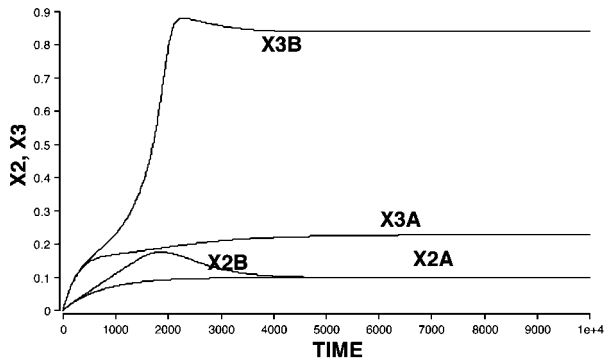
4. The response to step changes in feed flow rate, feed concentration or temperature may also be simulated.

### Results

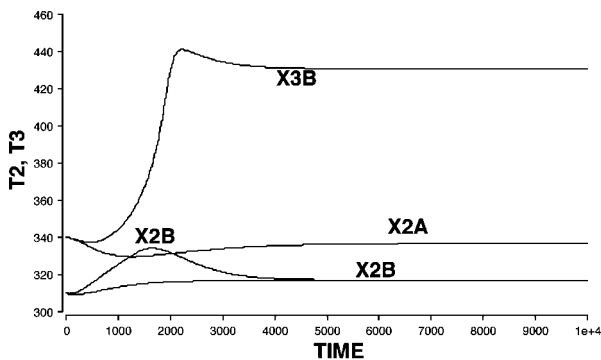
A change in the feed temperature will move the system to another steady state, as these results show.

### Reference

Mukesh, D. and Prasada Rao, C.D. (1977) *Ind. Eng. Chem. Proc. Des. Dev.* 16, 186.



**Fig. 2** A burst of warm feed at 310 K for the first 1400 seconds causes the system to shift into a higher temperature and higher conversion steady state. The fractional conversion curves A and C are for normal startup and B and D are for the startup with a warm feed period.



**Fig. 3** Temperature profiles corresponding to the conditions for Fig. 2. The curve labels are the same.

### 5.3.9

#### OSCIL – Oscillating Tank Reactor Behaviour

##### System

A water-cooled, continuous stirred-tank reactor is used to carry out the following exothermic parallel reactions.

The parameters used in the program give a steady-state solution, representing, however, a non-stable operating point at which the reactor tends to produce natural, sustained oscillations in both reactor temperature and concentration. Proportional feedback control of the reactor temperature to regulate the coolant flow can, however, be used to stabilise the reactor. With positive feedback con-

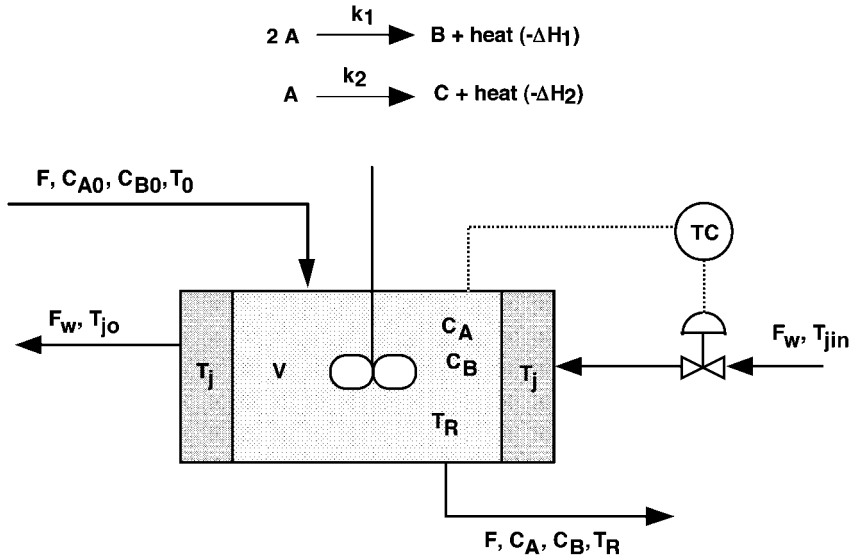


Fig. 1 Continuous tank reactor with coolant flow control.

control, the controller action reinforces the natural oscillations and can cause complete instability of operation.

### Model

The reaction kinetics are given by

$$r_A = -k_1 C_A^2 - k_2 C_A$$

and

$$r_B = k_1 C_A^2$$

The component mass balances become

$$V \frac{dC_A}{dt} = F(C_{A0} - C_A) - k_1 V C_A^2 - k_2 V C_A$$

$$V \frac{dC_B}{dt} = F(C_{B0} - C_B) + k_1 V C_A^2$$

where

$$k_1 = Z_1 e^{-E_1/RT_R}$$

and

$$k_2 = Z_2 e^{-E_2/RT_R}$$

The heat balance is given by

$$V\rho c_p \frac{dT_R}{dt} = F\rho c_p(T_0 - T_R) - UA(T_R - T_j) - k_1 V C_A^2(-\Delta H_1) - k_2 V C_A(-\Delta H_2)$$

Note that this includes terms for the rates of heat generation of both reactions. As shown in Section 1.2.5, the heat balance equation is equivalent to

$$V\rho c_p \frac{dT_R}{dt} = F\rho c_p(T_0 - T_R) - U'(T_R - T_{jin}) - k_1 V C_A^2(-\Delta H_1) - k_2 V C_A(-\Delta H_2)$$

where

$$U' = \frac{UAKF_w}{1 + KF_w}$$

and

$$K = \frac{2c_{pc}\rho_c}{UA}$$

Both the effects of coolant flow rate and coolant inlet temperature are thus incorporated in the model.

The effective controller action is represented by its effect on  $U'$  and hence on  $F_w$ , where

$$U' = U'_0 + K_c(T_R - T_{set})$$

Here  $K_c = 0$  represents open loop conditions,  $K_c < 0$  represents positive feed back conditions, and  $K_c > 0$  represents conventional negative feedback control.

### Program

The constant parameters for the program give a steady-state solution for the reactor, with the following conditions of

$$T = 333.4 \text{ K}, C_A = 0.00314, C_B = 0.000575 \text{ mol/cm}^3$$

but the system at this steady-state condition is unstable, and the simple open loop system of the reactor with no imposed controller action is such that the reactor itself generates sustained oscillations, which eventually form a limit cycle.

The program can be used to generate time dependent displays of  $C_A$ ,  $C_B$  and  $T_R$  for input values of the effective proportional gain  $K_C$  and set point temperature  $T_{SET}$ , for initial conditions  $C_{A0} = C_{B0} = 0$ ,  $T = T_0$  at  $t = 0$ .

Dimensionless variables are defined in the program, where

$$\bar{C}_A = \frac{C_A}{C_{A[\text{steady} - \text{state}]}} , \bar{C}_B = \frac{C_B}{C_{B[\text{steady} - \text{state}]}} \text{ and } \bar{T}_R = \frac{T_R}{T_{R[\text{steady} - \text{state}]}}$$

as these are useful in the following phase-plane analysis.

## Nomenclature

### Symbols

A	Heat transfer area	$m^2$
C	Concentration	$kmol/m^3$
$c_p$	Specific heat	$kJ/kg\ K$
$\Delta H$	Exothermic heat of reaction	$kJ/kmol$
E	Activation energy	$kJ/kmol\ K$
F	Volumetric flow rate	$m^3/s$
k	Rate coefficient	$1/s$
$K_c$	Controller constant	$kJ/m^2\ K^2$
$\rho$	Density	$kg/m^3$
T	Temperature	K
U	Heat transfer coefficient	$kJ/m^2\ K$
U'	Heat transfer conductance factor	$kJ/s\ K$
V	Volume	$m^3$
Z	Frequency factor	$1/s$

### Indices

A and B	Refer to components
1 and 2	Refer to reactions
0	Refers to inlet
j	Refers to jacket
in	Refers to inlet
O	Refers to outlet
R	Refers to reactor
w	Refers to coolant water

### Exercises

1. Study the simple, open-loop ( $KC = 0$ ) and closed-loop responses ( $KC = 1$  to  $5$ ,  $TSET = TDIM$ , and  $300$  to  $350$  K) and the resulting yields of B. Confirm the oscillatory behaviour and find appropriate values of  $KC$  and  $TSET$  to give maximum stable and maximum oscillatory yield. For the open-loop response, show that the stability of operation of the CSTR is dependent on the operating variables by carrying out a series of simulations with varying  $T_0$  in the range  $300$  to  $350$  K.
2. Make a dimensionless phase-plane display of  $BDIM$  versus  $ADIM$ , repeating the studies of Exercise 1. Note that the oscillatory behaviour tends to form stable limit cycles in which the average yield of B can be increased over steady-state operation.

### Results

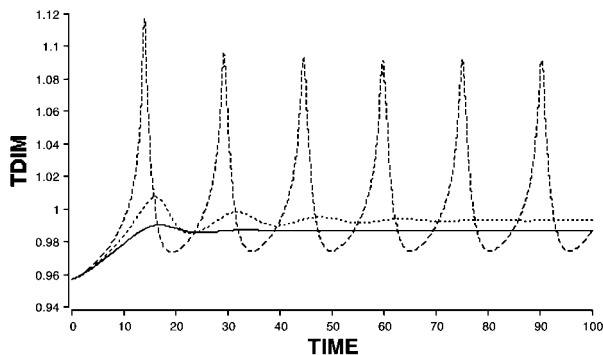


Fig. 2 Dynamic response of dimensionless temperature versus time for three setpoints;  $TSET = 325, 350$  and  $375$  K.

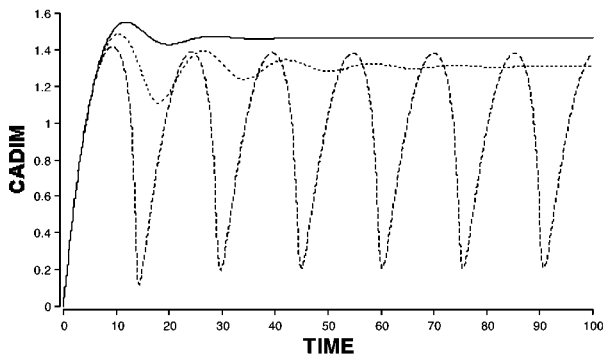


Fig. 3 Response of dimensionless concentration of A for the conditions of Fig. 2.

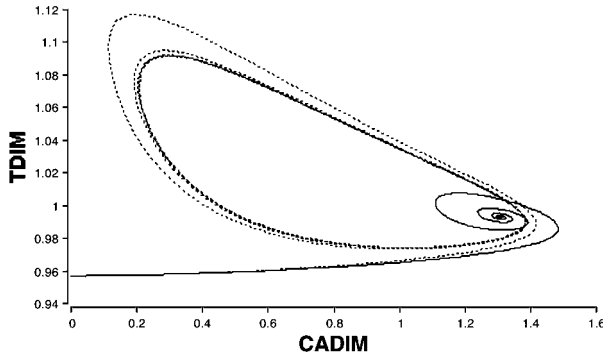


Fig. 4 A phase-plane plot of dimensionless CA versus dimensionless temperature for TSET = 325 and 350 K.

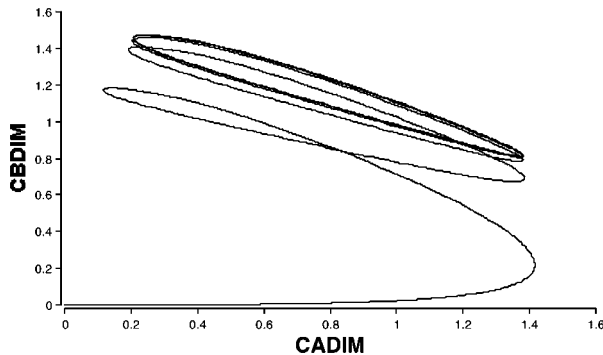


Fig. 5 A phase-plane plot of dimensionless concentrations of A and B for TSET = 350 K.

## Reference

Dorawala, T.G. and Douglas, J.M. (1971) *A.I.Ch.E.J.* 17, 974.

### 5.3.10

#### REFRIG1 and REFRIG2 – Auto-Refrigerated Reactor

#### System

In the auto-refrigerated reactor shown below, an exothermic reaction  $A \rightarrow B$  is carried out using a low-boiling solvent C. The heat of reaction is removed from the reactor by vapourising the solvent, condensing the vapour in the reflux condenser and returning the condensate as saturated liquid to the reactor. The total holdup of liquid in the reactor is maintained constant, but the temperature of the reactor is controlled by regulating the mass flow of vapour to the condenser. The example is taken from the paper of Luyben (1960).

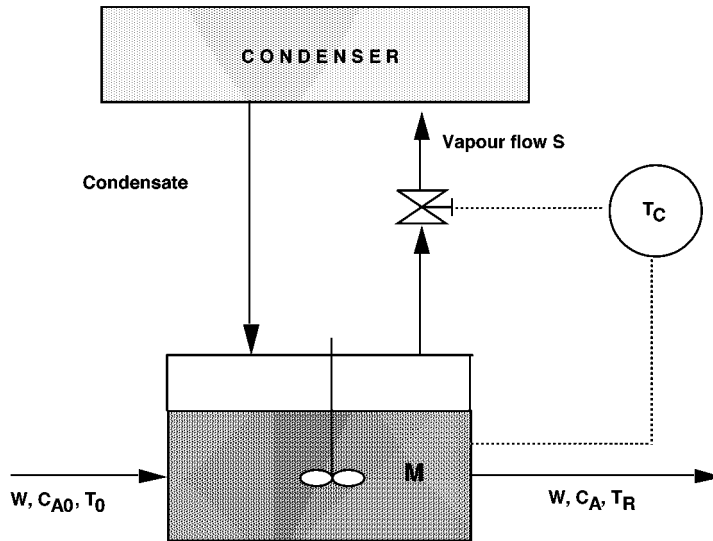


Fig. 1 A schematic drawing of the example REFRIG, showing control of the vapour rate.

### Model

The balance equations are as follows:

Component balance equation

$$M \frac{dC_A}{dt} = W(C_{A0} - C_A) - k C_A M$$

Energy balance equation

$$M c_p \frac{dT_R}{dt} = W c_p (T_0 - T_R) - M k C_A (-\Delta H_R) - S \Delta H_v$$

Arrhenius equation

$$k = Z e^{-E/RT_R}$$

Control equation

$$S = S_0 - K_P (T_{Set} - T_R)$$

At steady-state conditions

$$\frac{dC_A}{dt} = \frac{dT_R}{dt} = 0$$



$$\begin{pmatrix} \text{Rate of} \\ \text{generation} \\ \text{of heat} \end{pmatrix} = \begin{pmatrix} \text{Rate of} \\ \text{heat} \\ \text{removal} \end{pmatrix}$$

$$H_G = H_L$$

where

$$H_G = -M C_A k(-\Delta H_R)$$

and

$$H_L = W c_p(T_R - T_0) + S \Delta H_v$$

From the mass balance

$$C_A = \frac{C_{A0}}{1 + \frac{Mk}{W}}$$

### Program

The program **REFRIG1** calculates the steady-state heat generation and heat loss quantities,  $H_G$  and  $H_L$ , as functions of the reactor temperature,  $T_R$ , over the range 320 to 410 K. It is shown that, according to the van Heerden steady-state stability criterion that the simple loop control response,  $K_P = 0$  is unstable.

Program **REFRIG2** simulates the dynamic behaviour of the reactor and generates a phase-plane stability plot for a range of reactor concentrations and temperatures.

### Nomenclature

#### Symbols

$M$	Mass of reactor contents	kg
$C_A$	Reactant concentration	kg/kg
$t$	Time	h
$W$	Mass flow rate	kg/h
$k$	Kinetic rate constant	1/h
$c_p$	Specific heat	kJ/kg K
$T_0$	Feed temperature	K
$T_R$	Reactor temperature	K
$\Delta H_R$	Exothermic heat of reaction	kJ/kg
$S$	Vapour reflux rate	kg/h
$\Delta H_v$	Latent heat of vapourisation	kJ/kg
$Z$	Frequency factor	1/h
$E$	Activation energy	J/mol

R	Ideal Gas Constant	J/mol K
$S_0$	Base level for vapour rate	kg/h
$K_P$	Controller gain	kg/h K
$T_{Set}$	Set point temperature	K
$H_G$	Net rate of heat generation	kJ/h
$H_L$	Net rate of heat loss	kJ/h

### Exercises

- Using program REFRIG1, find the magnitude of the steady-state vapourisation rate,  $S_0$ , required to give stable operation.
- Using the value of  $S_0 = 330$  kg/h, use program REFRIG2 to find the value of the proportional gain constant  $K_P$  required to give stability.

### Results

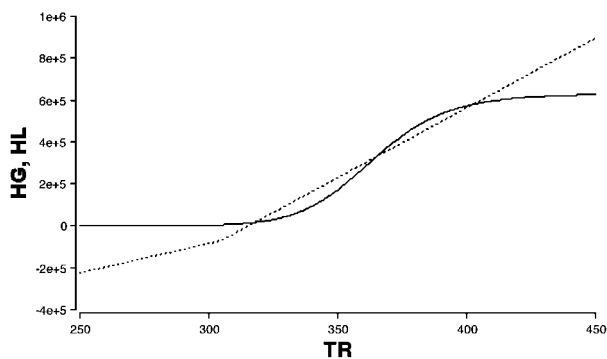


Fig. 2 Using REFRIG1, the plot of heat-loss and heat-gain terms versus temperature exhibits the stable state for  $K_P = 6$ .

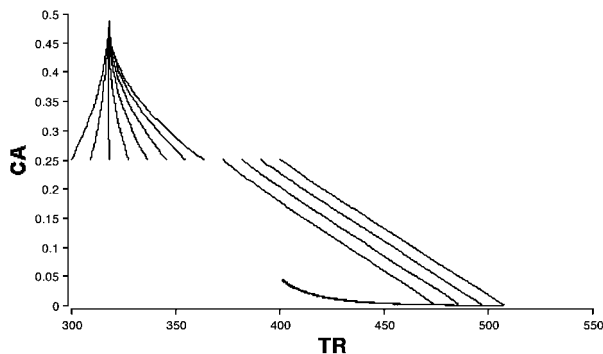


Fig. 3 Plots of the concentration-temperature phase-planes, corresponding to the conditions of Fig. 2 using REFRIG2.

## Reference

Luyben, W. L. (1960) A.I.Ch.E.J, 12, 663.

### 5.3.11

#### REVTEMP – Reversible Reaction with Variable Heat Capacities

#### System

A reversible reaction  $A \xrightleftharpoons[k_2]{k_1} B$  is carried out in a well-mixed, tank reactor, which can be run in either batch or continuous mode. A high temperature at the beginning of the batch will increase the rate of approach to equilibrium, while a low temperature at the end of the run will give a favourable final equilibrium condition. After starting the reactor under adiabatic conditions, there will be therefore an optimal time to turn on the cooling water. A heat exchanger is used for temperature control. This example is important in understanding the application of the energy balance and related thermodynamic considerations in the simulation of complex reactions with associated heat effects. This simulation example is also used in Section 2.4.1.1, Case A, to demonstrate the application of optimization to dynamic models.

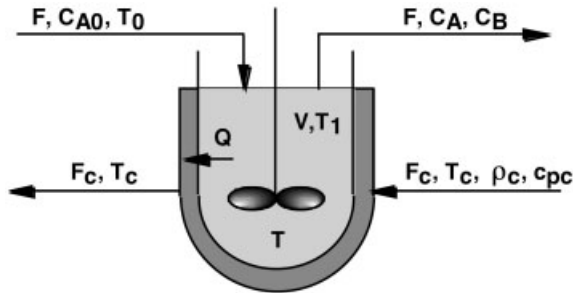


Fig. 1 Continuous stirred-tank reactor with cooling.

#### Model

##### Thermodynamics

The standard heat of reaction can be calculated from the heats of formation as

$$\Delta H_{RSt} = H_{FBSt} - H_{FASt}$$

The specific heats of reactant and product depend on temperature, according to

$$c_{pA} = a_A + b_A T$$

$$c_{pB} = a_B + b_B T$$

The equilibrium constant for the reaction at standard conditions is

$$K_{\text{Est}} = \frac{C_{\text{BE}}}{C_{\text{AE}}}$$

and its temperature dependency is given by the van't Hoff Equation

$$\frac{d \ln K_E}{dT} = \frac{\Delta H_R(T)}{RT^2}$$

where  $\Delta H_R$  at any temperature is calculated by

$$\Delta H_R = \Delta H_{\text{RSt}} + \int_{T_{\text{St}}}^T (c_{pB} - c_{pA}) dT$$

Therefore

$$\Delta H_R = \Delta H_{\text{RSt}} + (a_B - a_A)(T - T_{\text{st}}) + \frac{b_B - b_A}{2}(T^2 - T_{\text{st}}^2)$$

or with

$$\Delta H_{\text{RSt1}} = \Delta H_{\text{RSt}} - (a_B - a_A)T_{\text{st}} - \frac{b_B - b_A}{2}T_{\text{st}}^2$$

this reduces to

$$\Delta H_R = \Delta H_{\text{RSt1}} + \Delta a T + \frac{\Delta b}{2} T^2$$

where  $\Delta a = a_B - a_A$  and  $\Delta b = b_B - b_A$ .

Integration of the van't Hoff Equation then gives

$$\ln K_E = \ln K_{\text{Est}} - \frac{\Delta H_{\text{RSt1}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{St}}} \right) + \frac{\Delta a}{R} \ln \frac{T}{T_{\text{St}}} + \frac{\Delta b}{R} (T - T_{\text{St}})$$

#### *Material Balance Equations*

The total mass balance, assuming constant density is

$$\frac{d(\rho V)}{dt} = 0$$

Thus  $V$  is a constant under constant density conditions.

The component balances are given by

$$V \frac{dC_A}{dt} = -F(C_{A0} - C_A) + r_A V$$

$$V \frac{dC_B}{dt} = -F C_B + r_B V$$

The kinetics are each assumed to be first order, where  $r_A = k_1 C_A$  and  $r_B = k_2 C_B$

At equilibrium

$$k_1 C_{AE} = k_2 C_{BE}$$

Since

$$K_E = \frac{C_{BE}}{C_{AE}}$$

then

$$k_2 = \frac{k_1}{K_E}$$

which allows the kinetics to be written as

$$r_A = -r_B = -k_1 \left( C_A - \frac{C_B}{K_E} \right)$$

The kinetic rate constant  $k_1$  is a function of temperature according to

$$k_1 = k_{A1} e^{-E_1/RT_1}$$

### Energy Balance Equations

The reactor energy balance as derived in Section 1.2.5 is

$$\sum_{i=1}^2 n_i c_{pi} \frac{dT_1}{dt} = F_0 \sum_{i=1}^2 C_{i0} \int_{T_1}^{T_0} c_{pi} dT_1 - \Delta H_R r_A V + U A (T_c - T_1)$$

The individual terms are now

$$a = \sum_{i=1}^2 n_i c_{pi} = V(C_A(a_A + b_B T_1) + C_B(a_B + b_B T_1))$$

$$\beta = \sum_{i=1}^2 C_{i0} \int_{T_1}^{T_0} c_{pi} dT_1 = C_{A0}(a_A(T_0 - T_1) + \frac{b_A}{2}(T_0^2 - T_1^2))$$

$$\Delta H_R = \Delta H_{StR} + (a_B - a_A)(T_1 - T_{St}) + \frac{b_B - b_A}{2}(T_1^2 - T_{St}^2)$$

The energy balance for the reactor becomes

$$a \frac{dT_1}{dt} = F_0 \beta + \Delta H_R r_A V + U A(T_c - T_1)$$

The energy balance for the jacket is

$$V_c c_{pc} \rho_c \frac{dT_c}{dt} = F_c c_{pc} \rho_c (T_{c0} - T_c) - U A(T - T_c)$$

### Optimization

An objective function, SPTYB, is defined for batch operation

$$SPTYB = \frac{C_B^2}{T}$$

and for continuous operation

$$SPTYC = \frac{C_B^2 F}{V}$$

These functions represent space-time yields with special weightings for high conversion.

### Program

The reactor is run initially as a batch reactor ( $F = 0$ ) under adiabatic conditions ( $F_{C0} = 0$ ) to obtain a high initial rates of reaction. At time TIMEON the cooling flow rate is set to FCON and the reaction temperature reduced to obtain favourable equilibrium conditions.

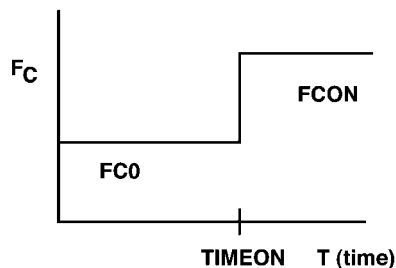


Fig. 2 Cooling flow rate profile.

## Nomenclature

### Symbols

A	Heat transfer area of jacket	$m^2$
C	Concentration	$mol/m^3$
$c_p$	Specific heat of vessel contents	$kJ/kg\ K$
$c_{pc}$	Specific heat of cooling water	$kJ/kg\ K$
$E_i$	Activation energy of reaction	$kJ/mol$
F	Flow rate to the reactor	$kg/s$
$F_c$	Coolant flow rate	$m^3/s$
$k_{A1}$	Arrhenius rate constant	$1/s$
$K_E$	Equilibrium constant	–
$k_i$	Reaction rate constant	$1/s$
N or n	Number of moles	mol
R	Gas constant	$kJ/mol\ K$
SPTYB	Objective function for batch operation	$mol^2/m^6\ s$
$T_1$	Temperature in reactor	K
$T_c$	Temperature of jacket contents	K
$T_{c0}$	Coolant supply temperature	K
U	Heat transfer coefficient	$kJ/s\ m^2$
V	Vessel volume	$m^3$
$V_c$	Jacket volume	$m^3$
$\Delta H_R$	Reaction enthalpy	$kJ/mol$
$\rho$	Density of vessel contents	$kg/m^3$
$\rho_c$	Density of cooling liquid	$kg/m^3$

### Indices

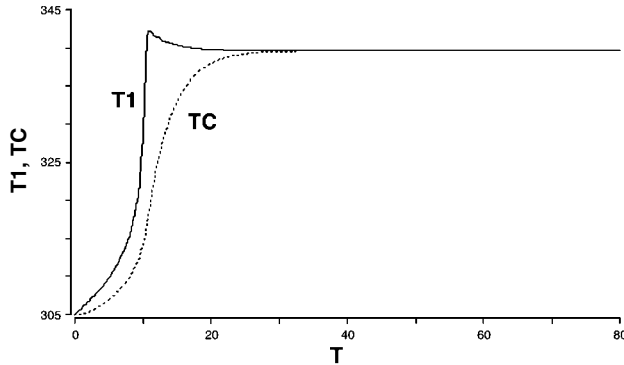
A	Indicates component A
B	Indicates component B
1	Refers to reaction $A \rightarrow B$
2	Refers to reaction $B \rightarrow A$
E	Refers to equilibrium
0	Refers to reactor inlet
St	Refers to standard conditions (298 K)

### Exercises

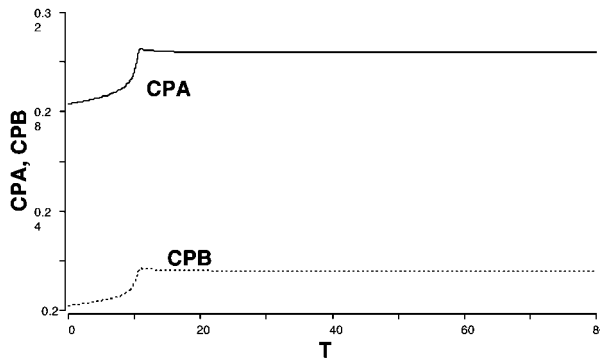
1. Compare the batch reactor performance at constant  $c_p$  with that for variable  $c_p$ . Do this by setting both  $c_p$  values constant at a temperature  $T_1$  and calculating  $c_{pi1} = a + b T_1$  for particular values of  $a_A = c_{pA1}$ ,  $a_B = c_{pB1}$ ,  $b_A = 0$  and  $b_B = 0$ .
2. Optimise the reactor performance (space-time yield SPTB) by varying the value of TIMEON. Compare results obtained with those in Section 2.4

3. Vary both F0 and FCON to obtain the optimum SPTYB.
4. Run the reactor continuously with continuous feed to and from the reactor. Observe the effect of varying space-time on the reaction yield and on SPTYC. Set TIMEON = 0, and to give continuous cooling set FCON to the desired cooling flow rate.

### Results



**Fig. 3** Temperature profiles for the batch reactor, T1, and for the jacket TC, which lags behind. No cooling, TIMEON = 1000.



**Fig. 4** Variation of the  $c_p$  values as a result of the temperature profiles, corresponding to Fig. 3.



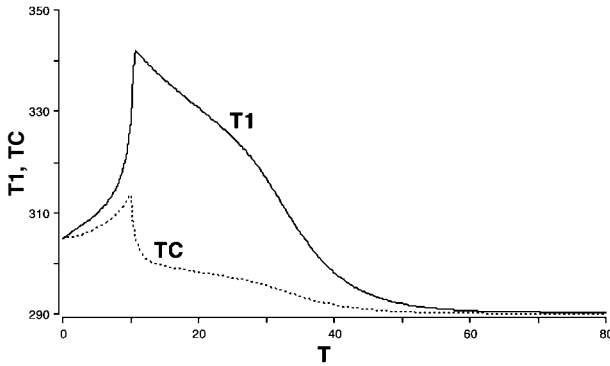


Fig. 5 Temperature profiles caused by turning on the cooling water flow by setting TIMEON to 10.

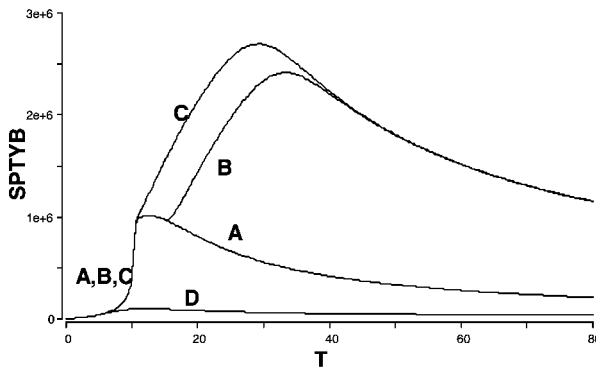


Fig. 6 Space-time yields, SPTYB, profiles in the batch reactor as a result of varying TIMEON (A – 1000, B – 15, C – 10, D – 5).

### 5.3.12

#### REVREACT – Reversible Reaction with Temperature Effects

##### System

A reversible reaction,  $A \xrightleftharpoons[k_2]{k_1} B$ , takes place in a well-mixed tank reactor. This can be operated either batch-wise or continuously. It has a cooling jacket, which allows operation either isothermally or with a constant cooling water flowrate. Also without cooling it performs as an adiabatic reactor. In the simulation program the equilibrium constant can be set at a high value to give a first-order irreversible reaction.

This example allows the study of the interaction of chemical reaction with temperature influence. Various cooling control strategies can also be simulated.

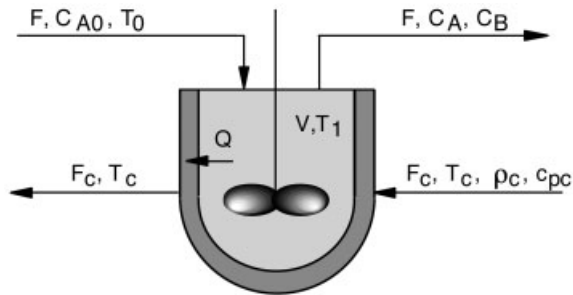


Fig. 1 Stirred-tank reactor with cooling

## Model

### Thermodynamics

The standard heat of reaction can be calculated from the heats of formation.

$$\Delta H_{RSt} = H_{FBS_t} - H_{FASt}$$

Here the heat capacities are assumed to be constant.

At equilibrium there is a fixed ratio of product to reactant.

$$K_{ESt} = \frac{C_{BE}}{C_{AE}}$$

The temperature dependence on the equilibrium constant is described by the van't Hoff Equation

$$\frac{d \ln K_E}{dT} = \frac{\Delta H_R(T)}{RT^2}$$

where the heat of reaction is assumed constant over the temperature range.

Integration of the van't Hoff Equation gives

$$\ln K_E = \ln K_{ESt} - \frac{\Delta H_{RSt}}{R} \left( \frac{1}{T} - \frac{1}{T_{St}} \right)$$

### Mass Balances

Density  $\rho$  and volume  $V$  are constant. The component balances are then.

$$V \frac{dC_A}{dt} = -F(C_{A0} - C_A) + r_A V$$

$$V \frac{dC_B}{dt} = -F C_B + r_B V$$

The kinetics are first order for both reactions such that  $r_1 = k_1 C_A$  und  $r_2 = k_2 C_B$ .

At equilibrium

$$k_1 C_{AE} = k_2 C_{BE}$$

Since

$$K_E = \frac{C_{BE}}{C_{AE}}$$

then

$$k_2 = \frac{k_1}{K_E}$$

giving

$$r_A = -r_B = -k_1 \left( C_A - \frac{C_B}{K_E} \right)$$

The kinetic rate constant  $k_1$  is a function of temperature according to

$$k_1 = k_{A1} K_1 = K_{A1} e^{-\frac{E_1}{RT_1}}$$

*Energy Balances*

For the reactor

$$\rho c_p V \frac{dT_1}{dt} = F_0 \rho c_p (T_0 - T_1) - \Delta H_R r_A V + U A (T_c - T_1)$$

Giving

$$\frac{dT_1}{dt} = \frac{F_0}{V} \rho c_p (T_0 - T_1) - \frac{\Delta H_R r_A}{\rho c_p} + \frac{U A}{\rho c_p V} (T_c - T_1)$$

For the well-mixed cooling jacket

$$\rho_c c_{pc} V_c \frac{dT_c}{dt} = F_c \rho_c c_{pc} (T_{c0} - T_c) - U A (T_c - T_1)$$

Giving

$$\frac{dT_c}{dt} = \frac{F_c}{V} (T_{c0} - T_c) - \frac{U A}{\rho_c c_{pc} V} (T_c - T_1)$$

**Program**

The program provides for simple switching from one operation to another by setting the corresponding variables. Batch (1 batch, 0 continuous); Isothermal (1 isothermal, 0 non isothermal); Adiabatic (1 no heat transfer, 0 with heat transfer)

**Nomenclature****Symbols**

A	Heat transfer area of jacket	$m^2$
C	Concentration	$mol/m^3$
$c_p$	Specific heat of vessel contents	$kJ/kg\ K$
$c_{pc}$	Specific heat of cooling water	$kJ/kg\ K$
$E_i$	Activation energy of reaction	$kJ/mol$
F	Flow rate to the reactor	$kg/s$
$F_c$	Coolant flow rate	$m^3/s$
$k_{A1}$	Arrhenius rate constant	$1/s$
$K_E$	Equilibrium constant	–
$k_i$	Reaction rate constant	$1/s$
N or n	Number of moles	mol
R	Gas constant	$kJ/mol\ K$
SPTYB	Objective function for batch operation	$mol^2/m^6\ s$
$T_1$	Temperature in reactor	K
$T_c$	Temperature of jacket contents	K
$T_{c0}$	Coolant supply temperature	K
U	Heat transfer coefficient	$kJ/s\ m^2$
V	Vessel volume	$m^3$
$V_c$	Jacket volume	$m^3$
$\Delta H_R$	Reaction enthalpy	$kJ/mol$
$\rho$	Density of vessel contents	$kg/m^3$
$\rho_c$	Density of cooling liquid	$kg/m^3$

**Indices**

A	Indicates component A
B	Indicates component B
1	Refers to reaction $A \rightarrow B$
2	Refers to reaction $B \rightarrow A$
E	Refers to equilibrium
0	Refers to reactor inlet
St	Refers to standard conditions (298 K)

## Exercises

1. Investigate an isothermal, batch reactor (Set batch=1 und isothermal=1) with an irreversible first-order ( $k_1 \gg k_2$ ). For this purpose set KEST to a very high value, say  $1e20$ . Determine the necessary reaction time to achieve a fraction conversion, XA, of 90, 95 und 99%. Determine also the cycle time and the productivity. For this assume the down-time between batches is 30 min (1800 s). Perform this for two different temperatures between 300K and 320K.
2. Investigate an isothermal, continuous reactor (Set batch = 0 und isothermal = 1) with an irreversible first-order ( $k_1 \gg k_2$ ). For this purpose set KEST to a very high value, as in Example 1. Test whether at your temperature a steady-state is reached. If not then set the STOPTIME to a higher value. Determine what flow rate is required to give a 99% conversion. What residence times are required to give XA equal to 90, 95 und 99. Make a Parameter plot to show this. Using the same temperature as in Exercise 1 compare the residence times and productivities with the batch reactor case of Exercise 1.
3. Investigate the batch reactor for the case of an equilibrium reaction. Reset the equilibrium constant to the original value in the program. Run first the batch reactor isothermally in the range of 300 to 400 K and determine the equilibrium conversion. Use the Parameter Plot tool for this to obtain the values at each temperature. At low temperatures make sure the STOPTIME is always sufficiently long to reach equilibrium. Using the same temperatures as in Exercise 1, find the reaction times to achieve fraction conversions XA of 90, 95 und 99%.
4. Repeat the study of Exercise 3 but for a continuous reactor, as in Exercise 2.
5. Operate the batch reactor of Exercise 1 with a constant cooling water flowrate (Parameter batch = 1 und isothermal = 0): Flowrates: FC = 0, 0.02, 0.025 and 0.03. For each value of FC observe the profiles of T1, TC, XA. Zoom in to make observations on the initial phase of the reaction.

## Results

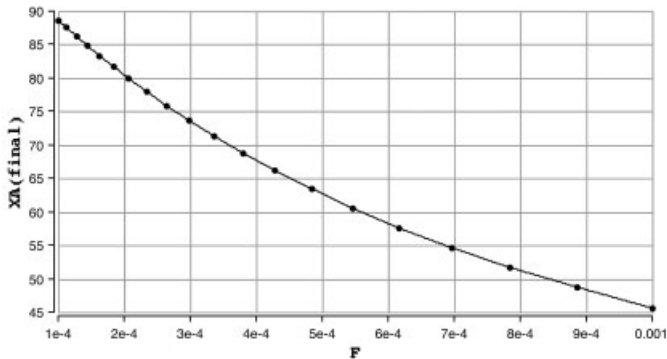


Fig. 2 Parameter plot showing variation of XA with F for the irreversible reaction run in an isothermal, continuous reactor at 305K

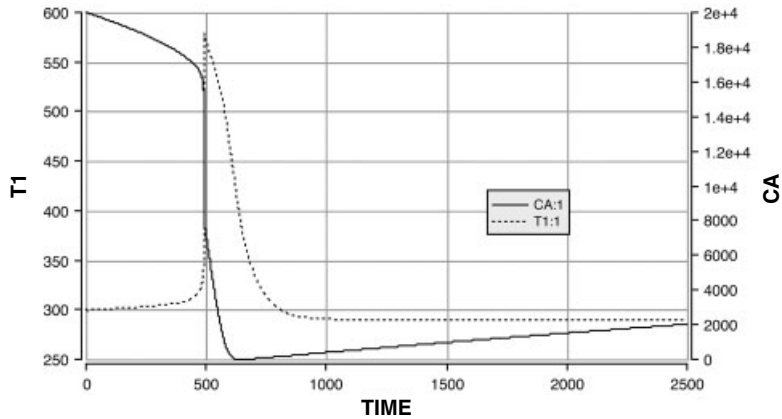


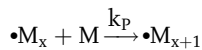
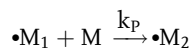
Fig. 3 The batch reactor with irreversible reaction and cooling water flow at  $0.023 \text{ m}^3/\text{s}$  gave these results.

### 5.3.13

#### HOMPOLY Homogeneous Free-Radical Polymerisation

##### System

A certain free-radical polymerisation reaction is described by the following sequence of initiation, addition and termination



The reaction is carried out in a non-cooled, continuous stirred-tank reactor (Fig. 1), and it is required to find the effect of changes in the reactor inlet conditions on the degree of polymerisation obtained. The model is that of Kenat, Kermode and Rosen (1967).

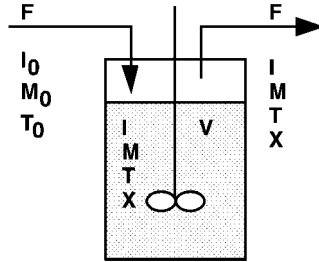


Fig. 1 The reactor for example HOMPOLY is a constant-volume stirred tank.

### Model

Only the propagation reactions are significantly exothermic and the energy balance is given by

$$\frac{dT}{dt} = \frac{F}{V}(T_0 - T) + \frac{-\Delta H_P}{\rho c_p} r_p$$

the monomer balance is represented by

$$\frac{dM}{dt} = \frac{F}{V}(M_0 - M) - r_p$$

and the initiator balance by

$$\frac{dI}{dt} = \frac{F}{V}(I_0 - I) - r_i$$

The reaction kinetics are as follows

- 1) Initiation or initiation decomposition reaction

$$r_i = 2f k_d I$$

where  $f$  is the fraction of free-radicals,  $\bullet R$ , initiating chains.

- 2) Termination  $r_t = 2k_t M^2$

- 3) Propagation  $r_p = k_p M M_0$

Assuming equal rates of initiation and termination

$$r_p = k_p \left( \frac{fk_d I}{k_t} \right)^{0.5}$$

The kinetic rate coefficients  $k_d$ ,  $k_t$  are described by Arrhenius temperature dependencies.

Average chain length

$$X = \frac{f_p}{r_i} = \left( \frac{k_p M}{f k_d k_t I} \right)^{0.5}$$

The model equations are expressed in dimensionless form and defining new variables in terms of the fractional deviation from steady state.

Dimensionless perturbation variables are defined as

$$\begin{aligned} T' &= \frac{T - \bar{T}}{\bar{T}} & M' &= \frac{M - \bar{M}}{\bar{M}} & I' &= \frac{I - \bar{I}}{\bar{I}} \\ F' &= \frac{F - \bar{F}}{\bar{F}} & X' &= \frac{X - \bar{X}}{\bar{X}} & \theta &= \frac{\bar{F}t}{V} \end{aligned}$$

where the bar superscripts relate to steady-state conditions, and the dash superscript represents the perturbation from steady state.

The model equations can then be recast into dimensionless form as

$$\frac{dT'}{d\theta} = \left( (T'_0 + 1) \frac{\bar{T}_0}{\bar{T}} - (T' + 1) \right) (F' + 1) + \left( 1 - \frac{\bar{T}_0}{\bar{T}} \right) (I' + 1)^{0.5} (M' + 1) \exp\left( E_2 \frac{T'}{1 + T'} \right)$$

$$\frac{dM'}{d\theta} = \left( (M'_0 + 1) \frac{\bar{M}_0}{\bar{M}} - (M' + 1) \right) (F' + 1) + \left( 1 - \frac{\bar{M}_0}{\bar{M}} \right) (I' + 1)^{0.5} (M' + 1) \exp\left( E_2 \frac{T'}{1 + T'} \right)$$

$$\frac{dI'}{d\theta} = \left( (I'_0 + 1) \frac{\bar{I}_0}{\bar{I}} - (I' + 1) \right) (F' + 1) + \left( 1 - \frac{\bar{I}_0}{\bar{I}} \right) (I' + 1) \exp\left( E_1 \frac{T'}{1 + T'} \right)$$

$$X' = \frac{(M' + 1)}{(I' + 1)^{0.5}} \exp\left( (E_2 - E_1) \frac{T'}{1 + T'} \right) - 1$$

In the above model equations, the terms  $\left( \frac{\bar{T}_0}{\bar{T}} \right)$ ,  $\left( \frac{\bar{M}_0}{\bar{M}} \right)$ ,  $\left( \frac{\bar{I}_0}{\bar{I}} \right)$ ,  $E_1$  and  $E_2$  now represent dimensionless constants, where

$$\left( \frac{\bar{M}_0}{\bar{M}} \right) = 1 + \frac{V A_p}{\bar{F}} \left( \frac{A_d \bar{I}}{A_t} \right)^{0.5} \exp(-E_2)$$

$$\left( \frac{\bar{T}_0}{\bar{T}} \right) = 1 - \frac{\bar{M}(-\Delta H_p)}{\bar{T} \rho c_p} \left( \frac{\bar{M}_0}{\bar{M}} - 1 \right)$$

$$\left( \frac{\bar{I}_0}{\bar{I}} \right) = 1 + \frac{V A_d}{\bar{F}} \exp(-E_1)$$

$$E_1 = \frac{E_d}{R \bar{T}}, \quad E_2 = \frac{2E_d + E_d - E_t}{2R \bar{T}}$$



For a full derivation of the above model equations, the reactor is referred to the original paper (Kenat et al., 1967).

### Program

The dimensionless model equations are programmed into the MADONNA simulation program HOMPOLY, where the variables, M, I, X and TEMP are zero. The values of the dimensionless constant terms in the program are realistic values chosen for this type of polymerisation reaction. The program starts off at steady state, but can then be subjected to fractional changes in the reactor inlet conditions,  $M_0$ ,  $I_0$ ,  $T_0$  and  $F$ , of between 2 and 5 per cent, using the IF-THEN-ELSE statement and parametric run facility. The value of TIME in the program, of course, refers to dimensionless time.

### Nomenclature

#### Symbols

A	Arrhenius constant	1/s or kmol/m <sup>3</sup> s
$c_p$	Specific heat	kJ/kg K
E	Energy of activation	kJ/kmol
F	Flow rate	m <sup>3</sup> /s
I	Initiator's concentration	kmol/m <sup>3</sup>
M	Monomer's concentration	kmol/m <sup>3</sup>
•M	Chain radical concentration	kmol/m <sup>3</sup>
$M_x$	Dead polymer chain of x units	kmol/m <sup>3</sup>
• $M_y$	Growing polymer chain of y units	kmol/m <sup>3</sup>
•R	Initiator free radical	kmol/m <sup>3</sup>
T	Absolute temperature	K
V	Reactor volume	m <sup>3</sup>
X	Average degree of polymerisation or chain length	–
f	Reactivity fraction for free radicals	–
k	Rate constant	1/s or m <sup>3</sup> /kmol s
r	Rate of reaction	kmol/m <sup>3</sup> s
t	Time	s
$\theta$	Dimensionless time	–
$\rho$	Density	kg/m <sup>3</sup>
$\Delta H_p$	Heat of reaction per monomer unit	kJ/kmol

#### Indices

d	Refers to decomposition of initiator
i	Refers to initiation process
p	Refers to propagation reaction
t	Refers to termination reaction
0	Refers to inlet

### Exercises

1. Use the program to study the effects of both positive and negative fractional changes in feed temperature, monomer and initiator concentration and feed flow rate. Compare your observations with the results and explanations of Kenat et al. (1967).
2. One of the main conclusions of Kenat et al. (1967) was that the largest changes in polymer mean-chain length occur from the effect of inlet temperature changes and also that, therefore, controlling inlet temperature, rather than reactor temperature, is beneficial to reactor performance. Test this out by simulation.

### Results

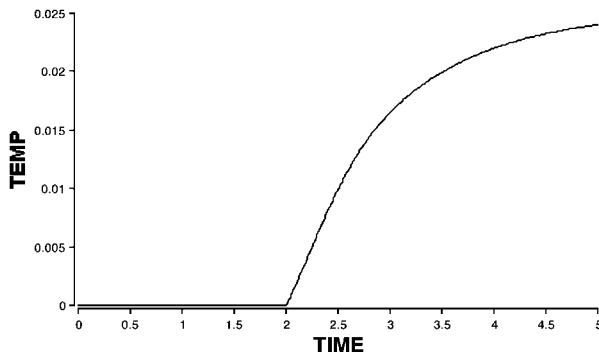


Fig. 2 An increase in the dimensionless feed temperature from 0 to 0.02 results in increased reactor temperature as shown.

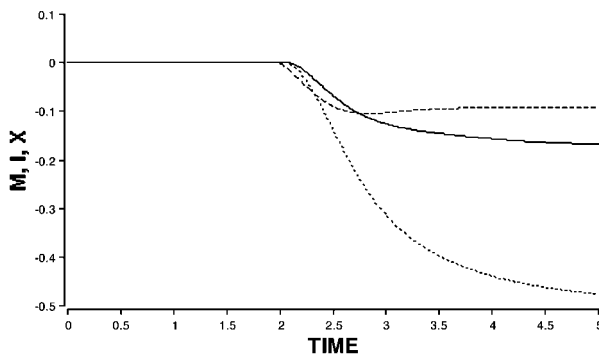


Fig. 3 The temperature change in Fig. 2 causes pronounced decreases in the dimensionless concentrations of monomer, initiator, and chain length.

### Reference

Kenat, T.A., Kermode, R.I. and Rosen, S.L. (1967) *Ind. Eng. Chem. Proc. Des. Devel.* 6, 363.