

Software functionality assessment for kinetic parameter estimation, model discrimination and design of experiments

I The four test cases

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Four case studies of kinetic parameter estimations were developed in order to create a thorough inventory of modeling packages suitable for parameter estimation and capable of describing two or more dimensional reactor models. These case studies cover a wide range of problems typically encountered in the chemical industries. Besides parameter estimation, the case studies require analyses of the estimation results by statistical tools and in some cases experimental design calculations are requested. This paper is a result of co-operation within Eurokin, a consortium of over 10 European companies and 4 universities.

Introduction

A survey, published by Bos et al. [1] indicated the need for improved methods to determine reaction kinetics within the chemical industry. Starting from this survey, the "EUROKIN" consortium has been established in 1998, comprising eleven companies and four universities.

Eurokin aims to produce a pre-competitive toolkit for measuring kinetic data and model development. The activities are focused on:

- Experimental methods to determine reaction kinetics; e.g. investigation of the capabilities of different types of laboratory reactors to measure the kinetics.
- Development of models for a set of selected laboratory reactor systems, to be used for processing experimental data, and/or the determination of suitable experimental conditions; e.g. assess if the proposed experimental conditions are in the kinetically or in the mass-transfer controlled regime.
- Methods for the determination of kinetic models from experimental data; including model discrimination, parameter estimation and design of experiments.

This paper describes the case studies developed to evaluate commercially available software packages for kinetic modeling with respect to their capabilities of parameter estimation, model discrimination and design of experiments. Aspects of user-friendliness are also assessed by evaluation of the case studies.

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Overview of the case studies

The case studies have been defined in such a way that most typical parameter estimation problems occurring in the industries and academia are covered with relative small and simple kinetic models. The experimental data for the case studies 1, 2 and 3 were created artificially with addition of realistic noise, the data presented in case study 4 were taken from a real experiment.

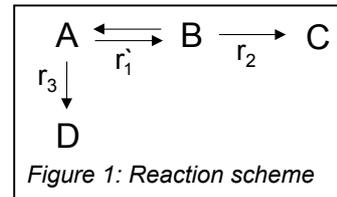
The cases are:

- 1) Estimation of the kinetic parameters in Langmuir - Hinshelwood - Hougen - Watson (LHHW) type rate equations, using experimental data sets obtained from a batch and a CSTR reactor.
- 2) Estimation of the kinetic parameters using experimental data and requiring a mass transfer limited, heterogeneous catalytic liquid phase reaction model, which comprises implicit algebraic and ordinary differential equations.
- 3) Investigation of the model discrimination and the design-of-experiments capabilities of the various software packages by means of twenty different rate equation models to describe a given set of experimental data.
- 4) Estimation of the kinetic parameters from experimental data obtained from the start-up of an industrial tubular reactor. This requires dynamic simulation of a tubular reactor, comprising a set of partial differential equations.

Case study 1

In this parameter estimation problem the data from four batch experiments and ten CSTR experiments have to be fitted.

The chemical system consists of four heterogeneously catalyzed reactions, see Fig. 1. The reaction between A and B is a reversible reaction (but not at equilibrium). The reaction rates are described with Langmuir-Hinshelwood Hougen-Watson equations. The species B is the desired product and C and D are undesired byproducts. Transport limitations do not occur.



For experiments in a batch reactor, the following differential material balance equations for A, C and D apply:

$$\frac{d[A]}{dt} = \frac{-k_1 K_A \left([A] - \frac{[B]}{K_{eq1}} \right) - k_3 K_A [A]}{1 + K_A [A] + K_B [B]}$$

$$\frac{d[C]}{dt} = \frac{k_2 K_B [B]}{1 + K_A [A] + K_B [B]} \quad \frac{d[D]}{dt} = \frac{k_3 K_A [A]}{1 + K_A [A] + K_B [B]}$$

where: $[i]$ = concentration of component i $[\text{mol} / \text{m}^3]$

k_i = (forward) reaction rate coefficient of reaction i $[\text{mol} / \text{m}^3 \text{ s}]$

K_J = adsorption constant of component J (A or B) on the catalyst $[\text{m}^3 / \text{mol}]$

K_{eq1} = thermodynamic equilibrium constant of reaction 1 (between A and B) $[-]$

In order to satisfy the material balance, it is recommended to calculate $[B]$ from the the material balance: $[B] = [A]_{initial} - [A] - [C] - [D]$.

The initial conditions at $t = 0$ are: $[A] = [A]_{initial}$ $[B] = 0$ $[C] = 0$ $[D] = 0$
 where: $[A]_{start}$ = concentration of component i at start-up (or $t = 0$) [mol / m^3]

The equilibrium constant, K_{eq1} and the adsorption constants K_A , K_B are described by:

$$K_{eq1} = 4.29 * 10^{-4} \frac{K_A}{K_B} \exp\left(\frac{30000}{R T}\right) \quad K_A = \exp\left(\frac{\frac{35000}{T} - 91}{R}\right) \quad K_B = \exp\left(\frac{\frac{20000}{T} - 53}{R}\right)$$

where: T = Temperature [K]
 R = Ideal gas constant = 8.314 [J / mol K]

The 'experimental' data were created by simulation and adding three types of noise to the data: (i) noise according to a heteroscedasticity of 1.5 with respect to the measured values, (ii) a manually added positive time shift of 5 to 8 seconds concerning the starting time of the batch experiments, and (iii) a small noise to the measurement times in the batch experiments. The second type of noise added resembles the generally occurring inaccuracy in the starting time of batch experiments. The generated data for four experiments in which initial concentrations of component A and temperatures are varied are shown in Table 1. A typical result of a batch experiment is shown in Fig. 2.

Table 1: 'Experimental' data for the four batch experiments (concentrations in mol/m^3).

Batch 1					Batch 2				
T= 330 K					T= 330 K				
[A] _{start} = 0.65					[A] _{start} = 1.10				
Time (s)	[A]	[B]	[C]	[D]	Time (s)	[A]	[B]	[C]	[D]
30	3.97E-01	2.33E-01	4.42E-03	3.76E-04	30	8.09E-01	2.99E-01	4.27E-03	4.92E-04
60	2.60E-01	3.74E-01	1.61E-02	6.32E-04	60	6.13E-01	4.69E-01	1.23E-02	6.96E-04
90	1.56E-01	4.65E-01	3.38E-02	7.97E-04	90	4.53E-01	6.20E-01	2.70E-02	1.03E-03
120	9.10E-02	5.03E-01	5.61E-02	7.41E-04	120	3.29E-01	7.63E-01	4.60E-02	1.16E-03
150	4.84E-02	5.13E-01	8.28E-02	8.66E-04	150	2.23E-01	8.01E-01	6.94E-02	1.18E-03
210	1.98E-02	4.89E-01	1.38E-01	8.37E-04	210	1.01E-01	8.57E-01	1.29E-01	1.40E-03
270	9.24E-03	4.38E-01	2.00E-01	1.02E-03	270	4.42E-02	8.68E-01	1.95E-01	1.58E-03
330	7.37E-03	3.83E-01	2.56E-01	1.06E-03	330	2.58E-02	8.12E-01	2.69E-01	1.73E-03
390	6.18E-03	3.33E-01	3.01E-01	1.07E-03	390	1.68E-02	7.35E-01	3.42E-01	1.71E-03
450	5.46E-03	2.92E-01	3.55E-01	1.04E-03	450	1.34E-02	6.90E-01	4.10E-01	1.64E-03

Batch 3					Batch 4				
T= 310 K					T= 360 K				
[A] _{start} = 1.10					[A] _{start} = 1.10				
Time (s)	[A]	[B]	[C]	[D]	Time (s)	[A]	[B]	[C]	[D]
30	1.03	7.58E-02	2.62E-04	5.79E-05	30	2.48E-01	7.90E-01	5.76E-02	3.38E-03
60	9.61E-01	1.39E-01	8.23E-04	9.54E-05	60	9.70E-02	8.58E-01	1.49E-01	4.22E-03
90	8.97E-01	2.02E-01	1.89E-03	1.79E-04	90	6.08E-02	7.90E-01	2.44E-01	4.36E-03
120	8.45E-01	2.56E-01	3.15E-03	1.98E-04	120	5.15E-02	7.17E-01	3.29E-01	4.81E-03
150	7.85E-01	3.04E-01	5.08E-03	2.32E-04	150	4.66E-02	6.44E-01	4.16E-01	5.29E-03
210	6.61E-01	4.29E-01	9.92E-03	3.48E-04	210	3.45E-02	4.86E-01	5.79E-01	5.87E-03
270	5.70E-01	5.13E-01	1.72E-02	3.51E-04	270	2.58E-02	3.62E-01	7.19E-01	6.35E-03
330	4.90E-01	5.98E-01	2.50E-02	4.93E-04	330	1.85E-02	2.57E-01	8.11E-01	7.08E-03
390	3.90E-01	6.77E-01	3.75E-02	4.94E-04	390	1.30E-02	1.78E-01	9.01E-01	7.53E-03
450	3.08E-01	7.41E-01	5.23E-02	5.86E-04	450	8.58E-03	1.35E-01	9.56E-01	7.02E-03

The rate parameters k_1 , k_2 and k_3 are to be estimated including confidence limits at each temperature (330, 310 and 360 K, resp.). It may be assumed that the values of k_1 and k_2 are within the range 0 - 0.1 and that of k_3 is within the range 0 - 0.001. It is necessary to fit the data for the concentration of component D, which is formed in only very small quantities, well. Since the absolute error in the observed

concentrations decreases almost proportionally with the values of these concentrations, an inverse proportional weighting of the squared errors*) should be applied according to: $Weight = 1/Y^n$ (with $Y =$ concentration of A, B, C or D at a particular time and use for the so-called heteroscedasticity factor n a value of 2, this corresponds to 'relative' weighting). Alternatively, also the heteroscedasticity factor n may be optimized (n should be between 0 and 2).

Temperature dependency

Subsequently, it is requested to estimate the temperature dependency of the rate parameters using Arrhenius type equations:

$$k_1 = k_1^0 \exp\left(\frac{-E_1}{R T}\right) \quad k_2 = k_2^0 \exp\left(\frac{-E_2}{R T}\right) \quad k_3 = k_3^0 \exp\left(\frac{-E_3}{R T}\right)$$

where: $k_i^0 =$ pre-exponential factor of reaction i [mol / m³ s]
 $E_i =$ activation energy of reaction i [J / mol]
 $R =$ gas constant = 8.314 [J / mol K]

Initial estimates of $k_1^0, E_1, k_2^0, E_2, k_3^0, E_3$ may be obtained from an Arrhenius plot^{#)}. With an efficient software package, the parameters should be possible to estimate directly from relatively bad initial estimates (e.g. choose 5E6 for k_1^0 and k_2^0 , 5E4 for k_3^0 and 5E4 for all E_a s).

In general it is not recommended to try to estimate the pre-exponential factors k_0 and the activation energies E_a using the standard Arrhenius expression since both parameters are strongly correlated, although it is a useful way to test the performance of the estimator. Instead, it is advised to re-parameterize the Arrhenius expressions according to:

$$\text{Original: } k = k_0 \exp\left(\frac{-E_a}{R \cdot T}\right) \quad \text{Re-parameterized: } k = k_{ref} \exp\left(\frac{-E_a}{R \cdot T^*}\right)$$

Where: $k =$ reaction rate coefficient

$k_0 =$ pre-exponential factor

$$k_{ref} = k_0 \exp\left(\frac{-E_a}{R \cdot T_{ref}}\right)$$

$T_{ref} =$ arbitrarily chosen reference temp. within the exper. temp. window

$T^* =$ re-parameterized temperature [K], obtained from the reactor temperature T [K] according to:

$$\frac{1}{T^*} = \frac{1}{T} - \frac{1}{T_{ref}}$$

For this case study one may use 330 K as the reference temperature and as the initial estimates $k_1^{330} = k_2^{330} = 0.05$, $k_3^{330} = 0.0005$, and $E_a = 50000$.

CSTR experiments

In practice, experiments are regularly performed in more than one reactor type, for example to reduce systematic experimental errors related to the reactor hardware. The kinetic parameters have to be estimated on basis of experimental data from the four batch reactor experiments and ten ideally continuously stirred tank reactor (CSTR) experiments.

The mass balance equations for the CSTR are:

*) Error = difference between measured concentration and concentration calculated using the model.

#) For construction of an Arrhenius plot: plot $\ln(k_i)$ versus T^{-1} ; the slope of the line obtained is equal to $-E_i/R$ and the value of $\ln(k_i)$ at $T^{-1} = 0$ gives the value of $\ln(k_i^0)$.

$$[A] = [A]_0 + \frac{\left[-k_1 K_A \left([A] - \frac{[B]}{K_{eq1}} \right) - k_3 K_A [A] \right] \tau}{1 + K_A [A] + K_B [B]}$$

$$[C] = \frac{(k_2 K_B [B]) \tau}{1 + K_A [A] + K_B [B]}$$

$$[D] = \frac{(k_3 K_A [A]) \tau}{1 + K_A [A] + K_B [B]}$$

where: τ = residence time in the reactor expressed in seconds [s]

The generated 'experimental' data for the 10 experiments at different temperatures, residence times and inlet concentrations of A are shown in the table below. The artificial noise added to the data was smaller than with the experimental data for the batch experiments.

Table 2: 'Experimental' data for the CSTR experiments (concentrations in mol/m³).

Experiment	$[A]_{start}$	$T(K)$	Residence time (s)	$[A]$	$[B]$	$[C]$	$[D]$
CSTR-1	0.35	330	90	1.01E-01	2.06E-01	3.97E-02	3.81E-04
CSTR-2	0.65	330	90	2.62E-01	3.46E-01	4.17E-02	5.97E-04
CSTR-3	1.1	330	30	8.86E-01	2.19E-01	4.34E-03	3.34E-04
CSTR-4	1.1	330	90	5.82E-01	4.86E-01	3.52E-02	7.68E-04
CSTR-5 *)	1.1	330	90	5.71E-01	4.84E-01	3.50E-02	7.78E-04
CSTR-6	1.1	330	150	4.15E-01	6.07E-01	8.38E-02	1.03E-03
CSTR-7	1.1	330	300	2.05E-01	6.53E-01	2.33E-01	1.40E-03
CSTR-8	2.4	330	90	1.72E+00	6.62E-01	2.08E-02	1.02E-03
CSTR-9	1.1	310	120	8.59E-01	2.33E-01	5.78E-03	1.77E-04
CSTR-10	1.1	360	45	3.84E-01	6.31E-01	9.06E-02	2.96E-03

*) Experiment CSTR-5 is a duplicate of experiment CSTR-4.

It is requested to estimate k_1 , k_2 and k_3 at 330 K using the results of experiments CSTR-1 – CSTR-8, and subsequently to estimate k_1^0 , E_1 , k_2^0 , E_2 , k_3^0 , E_3 using all ten CSTR experiments and all four batch experiments together. Since residence times are usually more accurate in CSTR experiments than in batch experiments, the data of the CSTR experiments should be given a 5 times higher weight than the data of the batch experiments.

Case study 2

In general, many kinetic researchers are not experienced modelers. As a result, they often struggle with models involving sets of implicit algebraic and ordinary differential equations, both for model simulation and parameter estimation. In order to test the capabilities of the various software packages to solve this kind of problems, a case study was defined using a mass-transfer limited, heterogeneous catalytic liquid phase reaction model, which comprises implicit algebraic and ordinary differential equations. The experimental data were created by performing simulations and by adding some noise to these data. The parameters corresponding to the proposed kinetic model should be estimated (optimized).

Reaction system

Component A reacts with B to form C , component C also reacts with A to form D , all reactions taking place in the liquid phase at the outer surface of spherical catalyst particles.

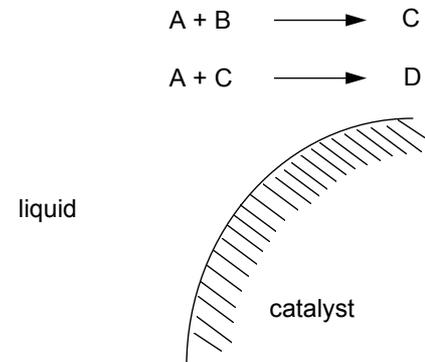


Fig. 3 Schematic representation of the reaction.

The kinetics can be described by:

Reaction of A with B to C :	$R_1 = \frac{k_1 K_{1m} K_{2m} [A]_s [B]_s}{\left(1 + \sqrt{K_{1m} [A]_s + K_{2m} [B]_s + K_{3m} [C]}\right)^3}$
Reaction of A with C to D :	$R_2 = \frac{k_2 K_{1m} K_{3m} [A]_s [C]}{\left(1 + \sqrt{K_{1m} [A]_s + K_{2m} [B]_s + K_{3m} [C]}\right)^3}$

The subscripts s for $[A]$ and $[B]$ denote concentrations at the surface of the catalyst. Mass transfer limitations in the liquid to solid film are an important factor in the overall process rate, so the surface concentrations will differ from those in the bulk of the liquid.

The experiments are performed in a fixed-bed reactor. The equations for the reactor in which experiments were performed are (R_1 and R_2 accordingly to the above expressions):

Eq. (1)	$\frac{d[B]}{dx} = -1442([B] - [B]_s)$	Eq. (3)	$9.88([A] - [A]_s) = (R_1 + R_2)$
Eq. (2)	$\frac{d[C]}{dx} = 28.8(R_1 - R_2)$	Eq. (4)	$\frac{1442}{28.8}([B] - [B]_s) = R_1$

The reactor length is denoted by x . The surface concentrations $[A]_s$ and $[B]_s$ are not measured. The boundary conditions: at $x = 0$: $[B] = [B]_0$ and $[C] = [C]_0$.

The concentration of A is kept constant over the reactor. Experiments were performed at one temperature; the residence time (length of the reactor), the concentration of A , and the feed concentrations of B and C were varied. The input data as well as experimentally observed concentrations of B , C and D at the outlet are shown in Table 3.

Table 3: 'Experimental' data for the 12 fixed-bed reactor experiments.

Experiment	Reactor length	$[A]$	$[B]_0$	$[C]_0$	$[D]_0$	$[B]$	$[C]$	$[D]$
1	0.165	2.67	25.39	3918	610.8	3.73	3914.1	636.3
2	0.165	2.67	50.78	3893	610.8	40.0	3901.6	613.0
3	0.165	2.67	76.17	3868	610.8	67.8	3875.7	611.5
4	0.232	2.67	25.39	3918	610.8	0.392	3904.3	649.5
5	0.232	2.67	50.78	3893	610.8	36.0	3901.1	617.4
6	0.232	2.67	76.17	3868	610.8	60.6	3881.6	612.7
7	0.165	10.68	25.39	3918	610.8	0.006	3849.6	704.5
8	0.165	10.68	50.78	3893	610.8	4.34	3923.0	627.2
9	0.165	10.68	76.17	3868	610.8	53.0	3888.8	613.1
10	0.232	10.68	25.39	3918	610.8	0	3796.3	757.9
11	0.232	10.68	50.78	3893	610.8	0.094	3870.0	684.4
12	0.232	10.68	76.17	3868	610.8	34.2	3903.0	617.7

The objective of this study is to find optimum values for the kinetic rate constants, k_1 , k_2 , K_{1m} , K_{2m} and K_{3m} on basis of the experimental data and to check the validity of results. Since the absolute error in the measured $[B]$ and $[D]$ is much smaller than that in $[C]$, $[C]$ was not measured but calculated from the mass balance via:

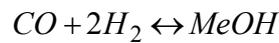
$$[C] = [B]_0 + [C]_0 + [D]_0 - [B] - [D]$$

Therefore, only $[B]$ and $[D]$ are required for the calculations. Ranges for initial guesses for the parameters should be confined to: $100 \leq k_1 \leq 1000$; $100 \leq k_2 \leq 1000$, $1 \leq K_{1m} \leq 10$; $0.1 \leq K_{2m} \leq 1$; $0.001 \leq K_{3m} \leq 0.01$. To verify whether the obtained optimum is a global one, repeat the optimization from other starting points.

The estimation of the rate parameters is not so easy since there is a significant correlation between the parameters. Since it is in practice hard to avoid the existence of correlations between (some of) the parameters, this is therefore a good test to check whether the estimator is capable to handle this.

Case study 3

A methanol synthesis problem has been used to investigate the model discrimination and the design-of-experiments capabilities. To simplify the problem, only the direct transformation of CO and H₂ into methanol has been considered:



Kinetic data have been generated for a CSTR reactor. This results in a data set, consisting of 27 reaction rates at different temperatures and partial pressures of the reactants. Duplicate experiments were included in the data set in order to allow an estimate of the variability within the data (these are experiments 17, 18 and 19).

Table 4: 'Experimentally' measured methanol formation rates as a function of temperature and the partial pressures of the components.

Exp.	T [K]	p _{CO} [bar]	p _{H2} [bar]	p _{MeOH} [bar]	r _{MeOH} [mol/g _{cat} /s]
1	495	40.0	84.0	10.0	4.789E-06
2	495	40.0	58.3	10.0	3.418E-06
3	495	15.1	84.0	10.0	4.447E-06
4	495	15.1	58.3	10.0	3.495E-06
5	495	40.0	84.0	2.50	7.174E-06
6	495	40.0	58.3	2.50	5.379E-06
7	495	15.1	84.0	2.50	6.662E-06
8	495	15.1	58.3	2.50	5.052E-06
9	475	40.0	84.0	10.0	1.254E-06
10	475	40.0	58.3	10.0	8.350E-07
11	475	15.1	84.0	10.0	1.150E-06
12	475	15.1	58.3	10.0	9.170E-07
13	475	40.0	84.0	2.50	2.005E-06
14	475	40.0	58.3	2.50	1.507E-06
15	475	15.1	84.0	2.50	2.045E-06
16	475	15.1	58.3	2.50	1.443E-06
17	485	25.0	70.0	5.00	2.858E-06
18	485	25.0	70.0	5.00	2.784E-06
19	485	25.0	70.0	5.00	2.793E-06
20	500	25.0	70.0	5.00	7.490E-06
21	470	25.0	70.0	5.00	9.900E-07
22	485	25.0	70.0	15.0	1.739E-06
23	485	25.0	70.0	1.70	3.725E-06
24	485	48.0	70.0	5.00	2.646E-06
25	485	12.6	70.0	5.00	2.552E-06
26	485	25.0	92.1	5.00	3.606E-06
27	485	25.0	53.0	5.00	2.271E-06

Twenty different, single rate equations were developed of varying complexity and form. Both the experimental data and the proposed rate equations were taken from Berty [2]. The rates are expressed in mol/(g_{cat} s).

1	$k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) p_C^{n_1} p_H^{n_2} p_M^{n_3}$	7	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) K_1 (K_2)^2 (p_C p_H^2 - p_M / K_{eq})}{(1 + K_1 p_C + K_2 p_H + K_3 p_M)^3}$
2	$k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - \frac{p_M}{K_{eq}}\right) p_C^{n_1} p_H^{n_2} p_M^{n_3}$	8	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) (p_C - p_M / (K_{eq} p_H^2))}{\left(1 + K_1 \frac{p_M}{K_{eq} p_H^2} + K_2 p_H + K_3 p_M\right)}$

3	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) p_C p_H^2}{(1+K_1 p_C)(1+K_2 p_H)(1+K_3 p_M)}$	9	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_H - \sqrt{p_M / (K_{eq} p_C)} \right)}{\left(1 + K_1 p_C + K_2 \sqrt{p_M / (K_{eq} p_C)} + K_3 p_M \right)}$
4	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) p_C p_H^2}{\left(1 + K_1 p_C + K_2 p_H^{0.5} + K_3 p_M \right)^5}$	10	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) K_3 \left(K_{eq} p_C p_H^2 - p_M \right)}{\left(1 + K_1 p_C + K_2 p_H + K_3 K_{eq} p_C p_H^2 \right)}$
5	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - p_M / K_{eq} \right)}{\left(1 + K_1 p_C + K_2 p_H^{0.5} + K_3 p_M \right)^5}$	11	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_H - \sqrt{p_M / (K_{eq} \cdot p_C)} \right)}{\left(1 + K_3 \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M \right)}$
6	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - \frac{p_M}{K_{eq}} \right)}{\left(1 + K_1 p_C + K_2 p_H + K_3 p_M \right)^3}$	12	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - p_M / K_{eq} \right)}{\left(1 + K_3 \cdot \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M \right) p_C p_H}$

13	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) p_C^{n_1} p_H^{n_2}}{\left(1 + K_1 p_C + K_2 p_H \right)^2}$
14	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - p_M / K_{eq} \right)}{\left(1 + K_2 \exp\left(\frac{-\Delta H_2}{RT^*}\right) p_H + K_3 \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M \right) p_C p_H}$
15	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - p_M / K_{eq} \right)}{\left(1 + K_1 p_C + K_3 \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M + K_4 p_H / p_C \right) p_C p_H}$
16	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - p_M / K_{eq} \right)}{\left(1 + K_1 \exp\left(\frac{-\Delta H_1}{RT^*}\right) p_C + K_2 \exp\left(\frac{-\Delta H_2}{RT^*}\right) p_H^{0.5} + K_3 \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M \right)^5}$
17	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - p_M / K_{eq} \right)}{\left(1 + K_1 \exp\left(\frac{-\Delta H_1}{RT^*}\right) p_C + K_2 \exp\left(\frac{-\Delta H_2}{RT^*}\right) p_H + K_3 \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M \right)^3}$
18	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) K_1 \cdot \exp\left(\frac{-\Delta H_1}{RT^*}\right) \cdot \left(K_2 \cdot \exp\left(\frac{-\Delta H_2}{RT^*}\right) \right)^2 \left(p_C p_H^2 - p_M / K_{eq} \right)}{\left(1 + K_1 \exp\left(\frac{-\Delta H_1}{RT^*}\right) \cdot p_C + K_2 \exp\left(\frac{-\Delta H_2}{RT^*}\right) p_H + K_3 \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M \right)^3}$
19	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) K_1 \exp\left(\frac{-\Delta H_1}{RT^*}\right) \left(K_2 \exp\left(\frac{-\Delta H_2}{RT^*}\right) \right)^2 \left(p_C p_H^2 - p_M / K_{eq} \right)}{\left(1 + K_1 \exp\left(\frac{-\Delta H_1}{RT^*}\right) p_C + K_2 \exp\left(\frac{-\Delta H_2}{RT^*}\right) p_H + K_3 \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M \right)}$
20	$\frac{k_{ref} \exp\left(\frac{-E_a}{RT^*}\right) \left(p_C p_H^2 - p_M / K_{eq} \right) p_C^{n_1} p_H^{n_2} p_M^{n_3}}{\left(1 + K_1 \exp\left(\frac{-\Delta H_1}{RT^*}\right) p_C + K_2 \exp\left(\frac{-\Delta H_2}{RT^*}\right) p_H + K_3 \exp\left(\frac{-\Delta H_3}{RT^*}\right) p_M \right)}$

where:

p_C	= partial pressure of CO	[bar]
p_H	= partial pressure of hydrogen	[bar]
p_M	= partial pressure of methanol	[bar]
T^*	= re-parameterized reaction temperature	[K]
T	= reaction temperature	[K]
K_{eq}	= thermodynamic equilibrium constant	[bar ⁻²]
k_{ref}	= rate coefficient at a reference temperature T_{ref} of 485 K	[mol/g _{cat} /s/bar ^x]
E_a	= activation energy	[J/mol]
K_i	= adsorption coefficient of product i at T_{ref}	[bar ⁻¹]
ΔH_i	= adsorption enthalpy of product i	[J/mol]
n_i	= apparent reaction order for product i	[-]
R	= ideal gas constant (= 8.3143)	[J/mol/K]

In these equations, the kinetic parameters are k_{ref} , E_a , K_1 , K_2 , K_3 , K_4 , ΔH_1 , ΔH_2 , ΔH_3 , n_1 , n_2 , and n_3 . The number of kinetic parameters varies from one rate equation to another. The re-parameterized reaction temperature T^* (in K) is calculated similarly as explained with Case study 1 with T_{ref} equal to 485 K. The equilibrium constant K_{eq} (in bar⁻²) is given as a function of the reaction temperature T (in K) by the following equation: $^{10}\log(K_{eq}) = 3914/T - 7.536 \ ^{10}\log T + 0.001766 T + 9.388$.

The general objective of the methanol case study is to select the most appropriate kinetic model. In order to do this, one should start with the estimation of the above listed rate equations on the basis of the experimental data. For the parameters, the following limits can be used : $0 \leq k_{ref} \leq 100$, $0 \leq E_a \leq 10^6$, $-10 \leq n_i \leq 10$, $0 \leq K_i \leq 10^{10}$, $-10^6 \leq \Delta H_i \leq 10^6$. The following initial parameter estimates may be used if necessary: $k_{ref} = 10^{-6}$, $E_a = 10^5$, $n_i = 0$, $K_i = 10^{-2}$, $\Delta H_i = 0$. It is recommended to repeat the optimization from other starting points in order to verify whether the obtained optimum is a global one. For each of the models, statistical tests on the model and on the various parameters should be performed in order to select the appropriate model(s) from the 20 models.

A ranking of models (best to worse) might be simply based on the sum of (weighted) squares obtained in the parameter estimation run. Preferably, this sum of squares is corrected by dividing this sum of squares by the number of degrees of freedom (calculated as the number of experimental data points minus the number of parameters estimated). It is recommended to create a model ranking using more accurate means such as one by using F-test values [2] or probability density functions.

Models may be rejected for three different reasons: (i) because the differences between the experimental data and the data calculated with the fitted model are much larger than the measurement error (the model is then qualified as 'inadequate'), (ii) because the fit of the model is significantly worse than an alternative model, and (iii) because one or more parameters in the kinetic model cannot be estimated accurately and independently, which usually indicates that the model contains too many parameters.

Design of experiments

This case study also allows assessment of the capabilities of software packages concerning the (sequential) design of experiments. It is requested to propose one or

several experiments to be carried out in order to improve model discrimination and/or to improve statistical significance of model parameters. Due to experimental constraints, the partial pressures and temperatures in experiments need to remain within the following limits: $10 < p_C < 50$ bar, $50 < p_H < 100$ bar, $0 < p_M < 15$ bar, $470 < T < 500$ K and $70 < p_{tot} < 140$ bar ($p_{tot} = p_C + p_H + p_M$).

Case study 4

A dynamic tubular reactor model, comprising a set of partial differential equations, is a test of computational efficiency and data handling capabilities of the various software packages. This model was originally published in 1992 [3]. Experimental data of three time-varying model inputs, i.e. the reactor temperature measured at several fixed reactor locations, the fluid velocity and the reactant inlet concentration, should be used to estimate the model parameters.

The plant reactor system consists of a feed mixer, a preheater and a series of seven horizontal vessels with baffles. The reactor is insulated and located outdoors in an open structure. Thermo-elements are located at several positions between reactor inlet ($z = 0$) and reactor outlet ($z = 1$). The relative position (z) of a thermo-element is calculated by taking the ratio of the volume from the reactor inlet up to the particular thermo-element and the total reactor volume, according to the model assumptions. The scheme of reactions carried out in the reactor is simplified to one overall reaction describing the consumption of the main reactant B :



This reaction is carried out in the liquid phase at pressures sufficiently high to avoid boiling. Reactant A is fed in excess, because reactant B should be totally converted at the reactor exit. The plant reactor is an adiabatic tubular reactor and its dynamic behavior can be described by three partial differential equations (PDE's). The equations are given in dimensionless forms. The mass balance for component B is:

$$\frac{\partial \Gamma_B}{\partial \sigma} = -\phi_v \cdot \frac{\partial \Gamma_B}{\partial z} + \frac{1}{Pe_{mr}} \cdot \frac{\partial^2 \Gamma_B}{dz^2} - Da_r \cdot e^{(\gamma \cdot (1 - \frac{1}{\theta}))} \cdot \Gamma_B$$

The reaction is exothermic, and the reactor vessel will be heated up by the fluid during startup. As a result the reactor vessel acts like a heat sink during startup and influences the dynamic behavior of the system. Therefore, the heat transfer between the fluid and the reactor vessel is taken into account in the model. The energy balance for the fluid is given by:

$$\frac{\partial \theta}{\partial \sigma} = -\phi_v \cdot \frac{\partial \theta}{\partial z} + \frac{1}{Pe_{hr}} \cdot \frac{\partial^2 \theta}{dz^2} - U^* \cdot Da_r \cdot (\theta - \theta_w) + \Delta \theta_{adr} \cdot Da_r \cdot e^{(\gamma \cdot (1 - \frac{1}{\theta}))} \cdot \Gamma_B$$

The energy balance for the reactor vessel, neglecting heat transport through the tube wall by conduction in the axial direction and heat losses to the surroundings, is given by:

$$\frac{\partial \theta_w}{\partial \sigma} = Da_r \cdot U^* \cdot \omega_h \cdot (\theta - \theta_w)$$

The initial conditions are:

$$\sigma = 0: \quad \Gamma_B(z, \sigma) = \Gamma_B(z, 0) = 0; \quad \theta(z, \sigma) = \theta(z, 0); \quad \theta_w(z, \sigma) = \theta_w(z, 0) = \theta(z, 0)$$

The boundary conditions are:

$$\sigma \geq 0 \text{ and } z = 0: \quad \Gamma_B(0, \sigma) = \psi_B \quad \theta(0, \sigma) = \nu_\theta$$

$$\sigma \geq 0 \text{ and } z = 1: \quad \frac{\partial^2 \Gamma_B}{\partial z^2} = \frac{\partial^2 \theta}{\partial z^2} = 0$$

Notation:

- σ = dimensionless time, [-]
- $\Gamma_B(z, \sigma)$ = dimensionless reactant B concentration at axial position z and time σ , [-]
- ϕ_V = dimensionless fluid velocity, [-]
- z = dimensionless reactor length, [-]
- Pe_{mr} = Péclet number for mass dispersion, [-]
- Pe_{hr} = Péclet number for heat dispersion, [-]
- Da_r = Damköhler number, [-]
- γ = dimensionless activation temperature, [-]
- $\theta(z, \sigma)$ = dimensionless reactor temperature at axial position z and time σ , [-]
- $\theta_v(z, \sigma)$ = dimensionless reactor vessel temperature at axial position z and time σ , [-]
- $\Delta\theta_{adr}$ = dimensionless adiabatic temperature rise, [-]
- ω_h = dimensionless heat capacity ratio, [-]
- ψ_B = dimensionless reactant B concentration at the reactor inlet ($z = 0$), [-]
- ν_θ = dimensionless reactor inlet temperature, [-]
- U^* = dimensionless heat transfer coefficient, [-]

The experimental data were collected during a reactor startup and is presented in Appendix 1. This data set contains the dimensionless time σ , the dimensionless fluid velocity ϕ_V , the dimensionless reactant B concentration at the reactor inlet ψ_B , the dimensionless reactor inlet temperature ν_θ , and the dimensionless reactor temperature $\theta(z, \sigma)$ at various axial reactor positions z .

Firstly, it is requested to perform a reactor simulation and to calculate (i) the reactor temperature profile $\theta(z, \sigma)$ as a function of time σ and

axial position z , (ii) the reactant B concentration profile $\Gamma_B(z, \sigma)$ as a function of time and axial position z , and (iii) the total amount of reactant B leaving the reactor at $z = 1$ over the entire period of operation. The model parameters for this simulation are:

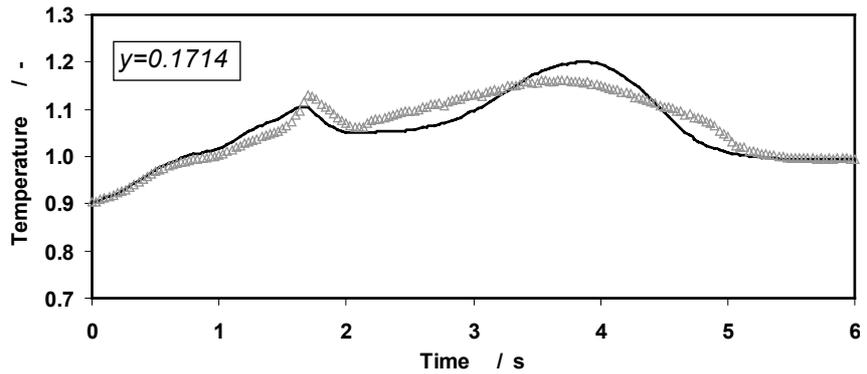


Fig. 4 Experimental data (triangles) and typical simulation result (continuous curve) at a relative axial position of 0.1714.

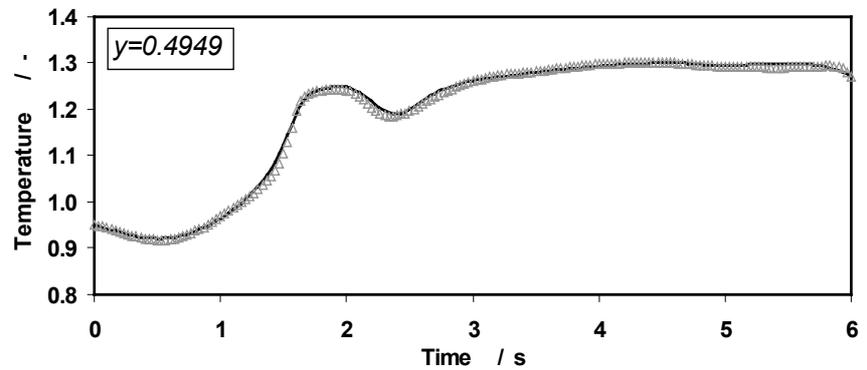


Fig. 5 Experimental data (triangles) and typical simulation result (continuous curve) at a relative axial position of 0.4949.

$\gamma = 20.2$, $Da_r = 0.41$, $Pe_{mr} = 196$, $Pe_{hr} = 42$, $U^* = 160$, $\Delta\theta_{adr} = 0.34$, $\omega_h = 11.67$. The model equations can be solved numerically by using a finite difference scheme for the partial derivatives in the axial dimension z using 501 (equidistant) grid points for the reactor length z . The initial temperature profile data $\theta(z,0)$ are presented in Appendix 2 for the fluid temperature $\theta(z,0)$ and the reactor wall temperature $\theta_w(z,0)$, the time varying data for the reactant B inlet concentration ψ_B are presented in Appendix 1 (column 1 + 3), the time varying data for the reactor inlet temperature v_θ are presented in Appendix 1 (column 1 + 4), and the time varying data for the fluid velocity ϕ_V are presented in Appendix 1 (column 1 + 2).

Aspects of special interest for the software packages are: (i) ease of implementation of the model in the software package, (ii) method of interpolation; how are the time varying inputs ψ_B , v_θ and ϕ_V used within the model, and (iii) the cpu time required for this simulation, taking into account the characteristics (processor, cash, memory) of computer hardware.

Parameter Estimation

Secondly, a parameter estimation run is requested where the objective is to find the optimum values for the following model parameters: $15 \leq \gamma \leq 25$, $0.1 \leq Da_r \leq 1$, $10 \leq Pe_{mr} \leq 250$, $10 \leq Pe_{hr} \leq 250$, $100 \leq U^* \leq 200$, using the experimental data presented in Appendix 1 and the initial temperature profile given in Appendix 2. The following initial parameter values may be used to start the parameter estimation run: $\gamma = 19$, $Da_r = 0.5$, $Pe_{mr} = 100$, $Pe_{hr} = 100$, and $U^* = 150$; while $\Delta\theta_{adr} = 0.34$ and $\omega_h = 11.67$.

By using 501 grid points to discretize the axial reactor position z , the temperatures calculated at the grid points shown in Table 5 should be used to estimate the indicated model parameters. Specific important aspects for this parameter estimation are (i) statistical tests on the model and on the various parameter estimates, (ii) the cpu time required.

Table 5: Grid points to be used in the parameter estimation.

$\theta(z, \sigma)$ experimental data	$\theta(\text{gridpoint})$ in the model
$\theta(0.1714, \sigma)$	$\theta(87)$
$\theta(0.3924, \sigma)$	$\theta(197)$
$\theta(0.4949, \sigma)$	$\theta(248)$
$\theta(0.5957, \sigma)$	$\theta(299)$
$\theta(0.6971, \sigma)$	$\theta(350)$
$\theta(0.7981, \sigma)$	$\theta(400)$
$\theta(0.8992, \sigma)$	$\theta(451)$
$\theta(1.0000, \sigma)$	$\theta(501)$

Outlook

The four parameter estimation test cases described in this paper are used to assess commercially available software packages for kinetic parameter estimation, model discrimination and design of experiments. Preliminary results already showed that none of the packages can be qualified as really good and user friendly. The results are communicated to the developers of the software packages in order to improve their products. A paper on the results of the assessment is in preparation.

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