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Sensitivity analysis based methodology to estimate the best set of parameters for heterogeneous kinetic models

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Abstract

The role of sensitivity analysis during kinetic parameter estimation is discussed in this work. An approach consisting in various steps: initialization of parameter values, nonlinear parameter estimation, and parameter sensitivity analysis, is proposed to assure that kinetic parameters are properly estimated and the convergence of the objective function to the global minimum is achieved. The method is illustrated with experimental data reported in the literature for the hydrodesulfurization of benzothiophene. The values of kinetic parameters obtained with the proposed methodology gave slightly lower values of the sum of square errors between experimental and predicted reaction rates compared with reported ones.

Keywords: Parameter estimation; Sensitivity analysis; Nonlinear regression

1. Introduction

Most of the mathematical models used for representing any type of phenomena (or situation) occurring not only during chemical reactions but also in other areas, e.g., thermodynamics, environmental sciences, molecular modeling, etc. involve parameters that need to be estimated from experimental data. The models can be supported on theoretical, semitheoretical/semiempirical or empirical bases, and their parameters can have theoretical meaning or be simply correlation constants [1]. Linear regression is the most-widely used method for parameter estimation due to its simplicity and easy manner to interpret the results, i.e., by representing the data in 2-dimension plots and examining how the experimental points deviate from the straight line. The common way that researchers often express the strength of the relationship between two variables is by the correlation coefficient (r) or determination coefficient (correlation coefficient squared, r^2), concepts from statistics, which are used to see how well trends in the predicted values follow trends in experimental values, and range between 0 and 1. If there is no relationship between the predicted values and the experimental ones $r = 0$, $r^2 = 0$ or are very low. As the strength of the relationship between the predicted values and experimental values increases, so does the correlation coefficient. A perfect fit gives a coefficient of 1. Thus, the higher the correlation and determination coefficients the better the fit [2].

Sometimes, a model can be transformed into different linear equations, such as in the case of Michaellis–Menten (M–M) model used in enzymatic kinetics, as can be seen in Table 1 [3–6]. It has been reported that the values of parameters of the M–M model calculated with the linear equations given in Table 1 can be slightly different, and it is recommended and more accurate to use that model which when representing the data in a 2-dimension plot gives better distribution of the experimental points along the straight line [7]. This has been confirmed by nonlinear regression analysis [8].

Another example of difficulties when using linear regression analysis to estimate kinetic parameters has been reported recently. For studying kinetics of hydrocracking of heavy oils in perfectly mixed continuously reaction system, some authors transform the resulting reaction rate equations in various straight lines as is presented in Table 2, and then they calculate separately the values of each parameter, k_0, k_1 and k_2 [9]. By this way, the condition $k_0 = k_1 + k_2$ is not satisfied, while when determining these kinetic parameters simultaneously by nonlinear regression this situation is not presented. The error between experimental and calculated yields has been shown to be lower

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Table 1
Example of different linear equations obtained from a same model

Method	Equation
Michaellis–Menten Model [5,7]	$v = \frac{V_{\max}[S]}{K_{\mathrm{m}} + [S]}$
Lineweaver and Burk [3]	$\frac{1}{v} = \frac{1}{V_{\max}} + \frac{K_{\mathrm{m}}}{V_{\max}} \frac{1}{[S]}$
Eadie–Hofstee [4]	$\frac{v}{[S]} = \frac{V_{\max}}{K_{\mathrm{m}}} - \left(\frac{1}{K_{\mathrm{m}}}\right) v$
Augustinsson [5]	$v = V_{\max} - K_{\mathrm{m}} \frac{v}{[S]}$
Woolf [6]	$\frac{[S]}{v} = \frac{K_{\mathrm{m}}}{V_{\max}} + \frac{1}{V_{\max}}[S]$
Nonlinear regression [1]	$\mathrm{SCE} = \sum \lvert(v^c - v^e)\rvert^2 = \sum_{i=1}^{N} \left\lvert \frac{V_{\max} C_s^e}{K_{\mathrm{m}} + C_s^e} - v^e \right\rvert$

Table 2
Example of parameter estimation with linear and nonlinear regression analyses

Kinetic model [9]	$\text{Feed } (A) \xrightarrow{k_1} \text{Light oils } (B)$ $\text{Feed } (A) \xrightarrow{k_2} \text{Gases } (C)$ $(r_A) = -(k_1 + k_2)C_A = -k_0 C_A$ $(r_B) = k_1 C_A$ $(r_C) = k_2 C_A$
Linear regression analysis (k_0, k_1 and k_2 are determined independently)	$\left(\frac{C_{A0} - C_A}{C_A}\right) = k_0 \left(\frac{1}{\mathrm{WHSV}}\right)$ $\left(\frac{C_{A0} - C_A}{C_A}\right)\left(\frac{C_B - C_{B0}}{C_A}\right) = k_1 \left(\frac{1}{\mathrm{WHSV}}\right)$ $\left[\frac{(C_{A0} - C_A)C_C}{C_{A0}C_A}\right] = k_2 \left(\frac{1}{\mathrm{WHSV}}\right)$
Nonlinear regression analysis (k_0, k_1 and k_2 are determined simultaneously)	$\mathrm{SSE} = \sum_{i=1}^{3} (C_i^{\mathrm{calc}} - C_i^{\mathrm{exp}})^2$ C_i^{calc} evaluated with the above equations

with parameter values determined with the latter approach [10].

As can be observed from the examples described above linear regression analysis can sometimes present problems when estimating parameters for a given model. That is why nonlinear regression is a more common approach when modeling of heterogeneous kinetic systems, in which the main objective is to optimize the values of the model parameters that provide the best fit to the experimental data. This nonlinear parameter estimation is carried out by using the least squares method, searching the best set of parameters that minimizes the sum of squares errors (SSE) between measured and calculated values [1,2].

When using nonlinear regression for parameter estimation, the task turns into a nonlinear optimization problem, which can be solved by optimization methods [11], such as Gauss–Newton, Levenberg–Marquardt among others. Levenberg–Marquardt method is of course the most popular alternative to the Gauss–Newton method of finding the minimum of a function that is a sum of squares of nonlinear functions. Some models, such as those used for describing heterogeneous kinetics, can have several parameters (sometimes hundreds) to be estimated, and be highly nonlinear; in those cases when determining the values of parameters, multiple solutions of the objective function during the optimization process (i.e. multiple minima) can be obtained and the best set of parameters is not guaranteed. The optimal solution depends mostly on the initial guess of parameters [12,13].

Most of the kinetics studies reported in the literature only give parameter values and r, r^2, residuals (differences between experimental and calculated values), absolute errors, or SSE, without enough evidence to assure that parameter values correspond to the global minima of the objective function, and consequently the model accuracy is not clearly established. The sensitivity analysis is a tool that allows for validating the values of parameters obtained by regression analysis. Sensitivity analysis is a way to assure that the solution of the objective function with a given set of parameters does correspond to the global minimum and not to local minima in the parameter optimization process [12]. It must be clarified that what is global is the minimum and not the sensitivity analysis, which is local. Although global convergence (i.e. global minimum) cannot be totally proved by a local sensitivity analysis, it is very helpful to obtain information about the surface of the model nearby the determined minimum, which most of the times coincide with global minima. Together with sensitivity analysis, previous experience with the particular case (e.g. knowledge about order of magnitude of the estimated parameters) also helps in establishing the accuracy of the estimated parameters.

Taking into consideration that sensitivity analysis in the fitting of kinetic data is a very important and until recently completely neglected topic, this paper proposes an approach based on sensitivity analysis to determine the best set of parameter values during parameters optimization process. The procedure is exemplified with parameter estimation of a heterogeneous kinetic model and experimental data of hydrodesulfurization of benzothiophene reported in the literature. This example was chosen due to the abundant experimental data reported by the authors, which by the way is not common to find in the open literature [14].

2. Description of the method

A direct and universal approach that can be a guarantee of the best solution during parameter estimation process is not easy to develop. The main difficulties when estimating parameters in heterogeneous kinetics are: the complexity of the model, which can be from simple algebraic equations to complex differential equation systems, linear or highly nonlinear in nature; the source and precision of experimental data, which can come from the literature (from one or more references) or from own or literature experiments specially designed to perform kinetic studies in which all the care has been put to assure kinetic regime; the robustness of the optimization algorithm, in most of the cases Levenberg–Marquardt method is used since it has shown to be superior over others [15]; the numerical method employed for solving the model equations, for instance, orthogonal collocation has been reported to fail for dynamic simulation of plug flow packed bed reactors and the method of characteristics has been preferred [16].

Therefore, what is presented here is not such a magic method but an approach that takes into consideration various steps, e.g., initialization of parameter values, nonlinear parameter estimation, and parameter sensitivity analysis, to determine and validate the set of parameters that minimizes the differences between experimental and calculated experimental values. A schematic representation of the proposed methodology is shown in Fig. 1.

2.1. Initialization of parameters

The optimal solution during nonlinear parameter estimation depends mostly on the initial guess of parameters values [12]. The initialization of parameters is a problem frequently found in nonlinear estimation that may converge to local minima and not to the global minimum during the parameter optimization process.

If the kinetic model and the corresponding parameters have been reported previously by other authors, no matter the differences in reaction conditions, catalyst, feed, reaction system, etc., at least the order of magnitude of the reported parameters values should be employed as initial guess. If there are not reported values, an iterative analysis of orders of magnitude of the parameters should be performed. This approach can sometimes be very tedious, since it implies the evaluation of the

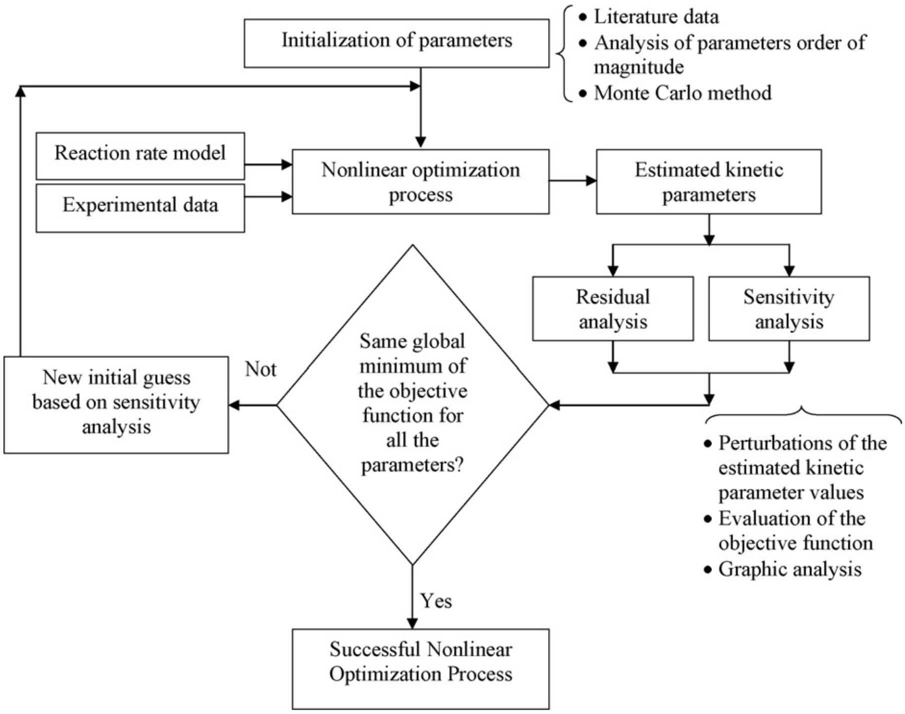

Fig. 1. Proposed methodology for parameter estimation.

objective function for different sets of parameters, starting say with $k_i = 1$ (where k is the parameter to be estimated, and $i = 1$, N parameters). Then, the value of each parameter is changed one at a time, say $k_j = 10$, keeping constant the values of the others ($k_i = 1$, for $i \neq j$), and the objective function is evaluated again. For any modification in the value of k_i the change in the objective function is examined and the influence of each parameter on the objective function (sensitivity of each parameter) is determined.

This procedure is repeated for different values of $k_i < 1$ (0.1, 0.01, 0.001, etc.) and/or $k_i > 1$ (10, 100, 1000, etc.) as many times as necessary. The lower the value of the objective function indicates the correct order of magnitude of the parameter value. This means that if one parameter is changed, for instance, from 1 to 10, and the value of the objective function increases, it is more likely that this parameter value is <1.

This approach allows for determining the order of magnitude of the parameter values and becomes easier the estimation of initial values. Of course, it requires patience and certain expertise in its use.

Initial guess of parameter values can also be obtained using Monte Carlo method [17], which consists mainly in the following steps: (1) initial guess of parameters is determined using random numbers, (2) with this initial guess of parameters the objective function (e.g. sum of square errors) is calculated, and (3) this procedure is repeated M times ($M > 1000$) and the minimum of the M values of the sum of squares of residuals is determined. The set of initial guess of parameters that corresponds to this minimum can be used as initial estimates in the nonlinear parameter optimization process.

2.2. Nonlinear parameter estimation

The reliable solution of nonlinear parameter estimation is an important computational problem when modeling of heterogeneous kinetic systems [15]. This nonlinear parameter estimation is commonly carried out by using the least squares method in order to find the global minimum of the following objective function:

$$\mathrm{SSE} = \sum_{i=1}^{N\,\mathrm{data}} (y_{\mathrm{exp}} - y_{\mathrm{calc}})^2 \tag{1}$$

The method of Marquardt [11] (also called Levenberg–Marquardt) uses the method of linear descent in early iterations and then gradually switches to the Gauss–Newton approach. Most of the scientific software (the so-called “solvers”) uses the Marquardt method for performing nonlinear regression analysis.

Most often nonlinear regression is done without weighting, giving equal weight to all points (as in Eq. (1)), as is appropriate when experimental scatter is expected to be the same in all parts of the curve. If experimental scatter is expected to vary along the curve, then the points can be weighted differentially. The most-often used weighting method is called “weighting by $1/y^2$” and is expressed as follows [18]:

$$\mathrm{SSE} = \sum_{i=1}^{N\,\mathrm{data}} \frac{1}{y_{\mathrm{exp}}^2} (y_{\mathrm{exp}} - y_{\mathrm{calc}})^2 \tag{2}$$

Sometimes, the data come with additional information about which points are more reliable. For example, different data may correspond to averages of different numbers of experimental trials, in this case weighting of the data should be added in the objective function to obtain better estimates

$$\mathrm{SSE} = \sum_{i=1}^{N\,\mathrm{data}} w_i (y_{\mathrm{exp}} - y_{\mathrm{calc}})^2 \tag{3}$$

where w_i is a weighting factor.

2.3. Sensitivity analysis

Sensitivity analysis is commonly employed to assess that in the nonlinear parameter estimation, the set of parameters does correspond to the global minimum and not to local minima [12]. Sensitivity analysis is applied to each of the estimated parameters by means of perturbations of the parameter value (keeping the other parameters in their estimated values). Perturbations are preferably done in the range of ±20%. For each perturbation in the parameter values the objective function is reevaluated and then for each parameter the perturbation percentage is plotted against the corresponding value of the objective function. If all perturbations in all the parameters give the minimum of the objective function with their original values (0% perturbation), then the global minimum has been achieved. On the contrary, if at least one parameter does not give the same minimum than the others at 0% perturbation, that means poor nonlinear parameter estimation. To correct this, the values of the wrong estimated parameters are re-determined by examining the sensitivity plot, and finally, parameter sensitivity is carried out again on these parameters and now the global minimum is guaranteed.

2.4. Residual analysis

Analysis of residual distribution, calculated as the difference between experimental and predicted values, is frequently practiced by some authors as a way to demonstrate that the estimated parameters for a given model accurately predict the experimental values. Plots of the residuals are used to check the quality of the fit. Graphical analysis of the residuals is the single most important technique for determining the need for model parameters refinement [19]. A plot of residual values against the number of experimental observations is commonly used, and a regular distribution of residuals with no prediction bias should be observed, thus proving the adequacy of the proposed model and the calculated parameters. On the contrary, if there is a pattern, the parameters are wrong estimated.

Residual analysis is certainly useful to see graphically the precision of estimations. However, it cannot guarantee by itself the achievement of the global minimum of the objective function. It is better to use both residual analysis and sensitivity analysis to assure that parameters are properly estimated.

2.5. Other approaches

In recent years, as computational power increases, other approaches in nonlinear parameter estimation have been developed. Simulated annealing (SA) is a global stochastic optimization method originated in the computational reproduction of the thermal process of annealing, where a material is heated and cooled slowly in order to reach a minimum energy state. In the SA method, starting from an initial configuration, a new configuration is generated randomly. If this new configuration has a smaller value of objective function (in a minimization context), then this new configuration will become the current configuration. Otherwise, a stochastic test is applied to indicate whether or not the new configuration will be accepted. This process of movement-acceptation is repeated, and as the number of analyzed alternatives increases, the acceptance probability of the worse configurations is gradually reduced. Due to the possibility of carrying out "wrong way" movements, the search can move from a local optimum toward the global optimum to avoid being trapped in a poor local solution [20,21].

The Grid Search Technique is another approach which retains the true nonlinearity of the model in the estimation of its parameters. In this method, a region for grid search is defined by specifying the lower the upper limits of the values of the kinetic parameters. The number of grid points in each direction is specified and the sum of the squares of residual between predicted and experimental values (SSR) obtained by using the parameters which characterize the grid point. This process is repeated until SSR is obtained for each grid point. Then the error surface (a three-dimensional representation of the sum of the squares of deviation) is drawn and is analyzed for its shape and the associated valley. The best set of parameters is then determined as the coordinates of that grid point which produced the lowest SSR [22].

Finally, in order to search for the global optimum, hybrid techniques have been proposed where a genetic algorithm (GA) is used to identify initial guesses and then a local optimizer is used to determine the optimum. Genetic algorithms are population based stochastic search procedures based on the survival of the fittest principle. A population of randomly generated solutions, i.e., parameter values for this problem, is progressively modified using genetic operators such as crossover and mutation in order to improve the population's fitness as measured by their effectiveness in predicting the experimental data. Of this way, genetic algorithms provide a potential tool for finding initial estimates in large parameter spaces, which followed by a traditional local optimization routine may be more efficient in searching for a global optimum [23].

3. Results and discussion

3.1. Experimental data and reaction rate model from the literature

Experimental data reported by Kilanowski and Gates [14] were employed to illustrate the application of the proposed methodology for parameter estimation. These data correspond to the hydrodesulfurization of benzothiophene conducted in a steady-state differential flow microreactor containing particles of sulfided $CoMo/Al_2O_3$ catalyst. The study was carried out at reaction temperatures of 252.5, 302 and 332.5 °C, and partial pressures in the following ranges: benzothiophene (BT), 0.015–0.23 atm; H_2, 0.20–2.0 atm; and H_2S, 0.02–0.14 atm. Differential conversion data were obtained to determine reaction rates directly. Catalyst deactivation was negligible over hundreds of hours of operation. A summary of experimental results is shown in Table 3.

Table 3
Summary of results of benzothiophene HDS kinetics [14]

T (°C)	P_{BT} (atm)	P_{H_2} (atm)	P_{H_2S} (atm)	P_{He} (atm)	r_{BT} ($\times 10^7$ gmol/g_{cat} s)
252.5	0.105	0.215	0.022	0.819	0.272
252.5	0.068	0.234	0.026	1.04	0.309
252.5	0.197	0.842	0.020	–	1.04
252.5	0.063	1.14	0.124	–	1.10
252.5	0.063	1.14	0.094	–	1.19
252.5	0.114	0.985	0.021	–	1.25
252.5	0.063	1.11	0.045	–	1.29
252.5	0.082	1.07	0.022	–	1.37
252.5	0.064	1.14	0.023	–	1.42
252.5	0.053	1.2	0.025	–	1.46
252.5	0.046	1.26	0.025	–	1.51
252.5	0.015	1.86	0.038	–	1.77
252.5	0.018	1.94	0.040	–	2.29
252.5	0.022	2.04	0.041	–	2.55
252.5	0.024	1.82	0.037	–	2.62
252.5	0.036	1.39	0.028	–	2.70
252.5	0.030	1.54	0.032	–	3.03
252.5	0.026	1.67	0.034	–	3.15
302	0.118	0.238	0.025	0.920	1.84
302	0.080	0.272	0.030	1.24	2.00
302	0.071	1.28	0.142	–	4.71
302	0.070	1.26	0.101	–	5.48
302	0.015	1.86	0.038	–	5.51
302	0.026	1.67	0.034	–	6.54
302	0.073	1.33	0.054	–	7.41
302	0.231	0.836	0.023	–	7.85
302	0.212	0.866	0.022	–	8.1
302	0.155	0.971	0.024	–	8.22
302	0.125	1.05	0.024	–	8.43
302	0.043	1.79	0.036	–	8.78
302	0.106	1.11	0.025	–	8.84
302	0.074	1.35	0.027	–	9.16
302	0.091	1.17	0.025	–	9.33
332.5	0.127	0.268	0.024	0.980	5.35
332.5	0.014	1.86	0.038	–	12.0
332.5	0.070	1.28	0.143	–	12.2
332.5	0.069	1.26	0.102	–	14.8
332.5	0.025	1.67	0.035	–	17.0
332.5	0.072	1.33	0.055	–	20.1
332.5	0.229	0.834	0.027	–	21.6
332.5	0.210	0.863	0.026	–	22.0
332.5	0.153	0.97	0.027	–	23.0
332.5	0.043	1.79	0.037	–	23.6
332.5	0.123	1.05	0.027	–	24.6
332.5	0.073	1.35	0.029	–	25.6
332.5	0.090	1.17	0.027	–	26.1
332.5	0.104	1.11	0.027	–	26.5

Kilanowski and Gates [14] also reported that the following Hougen–Watson kinetic models well represented the experimental information of hydrodesulfurization of benzothiophene.

At 252.5 °C:

$$r=\frac{kP_{\mathrm{BT}}P_{\mathrm{H_2}}}{(1+K_{\mathrm{BT}}P_{\mathrm{BT}}+K_{\mathrm{H_2S}}P_{\mathrm{H_2S}})^2} \tag{4}$$

At 302 °C and 332.5 °C:

$$r=\frac{kP_{\mathrm{BT}}P_{\mathrm{H_2}}}{(1+K_{\mathrm{BT}}P_{\mathrm{BT}}+K_{\mathrm{H_2S}}P_{\mathrm{H_2S}})(1+K_{\mathrm{H_2}}P_{\mathrm{H_2}})} \tag{5}$$

3.2. Initialization of parameters

Although in this case the authors have estimated and reported kinetic parameter values, they were not taken into account as first option as initial guess to give a better explanation of this step, and Monte Carlo method was employed instead.

First, an initial range of k_{i} values needs to be defined. A common range to be used for initial guess is 1–100. Fig. 2 shows the variation of the objective function (SSE) when random k_i values are employed. For illustration purposes only one hundred iterations with parameter k of the model given by Eq. (4) at 252.5 °C will be presented, but similar approach was followed for $K_{\mathrm{H_2S}}$ and K_{BT}. The lowest values of the SSE were found at also low k values, indicating that k is more likely to be in the direction of unity ($k\to 1$).

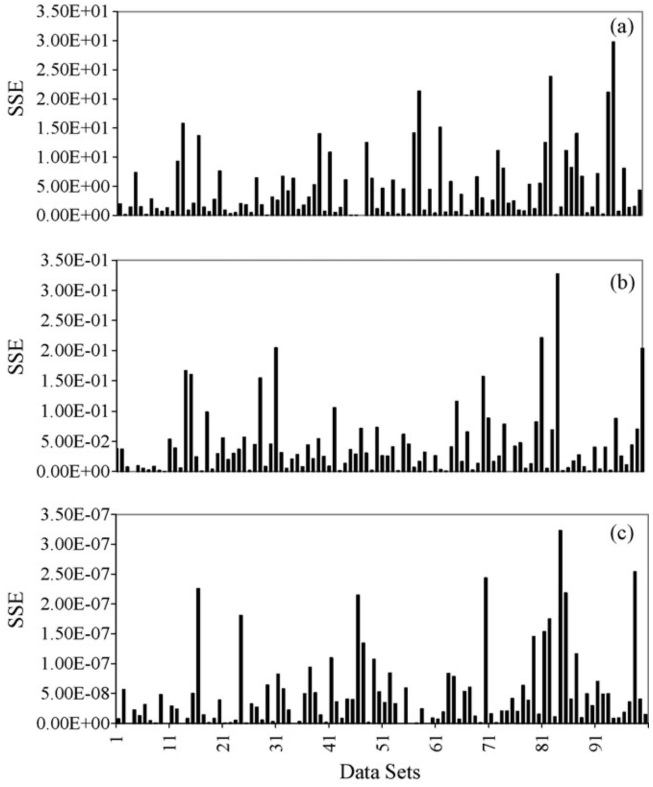

Fig. 2. Results of Monte Carlo simulation at 252.5 °C: (a) $1<k<100$, (b) $0.01<k<10$ and (c) $0.00001<k<0.001$.

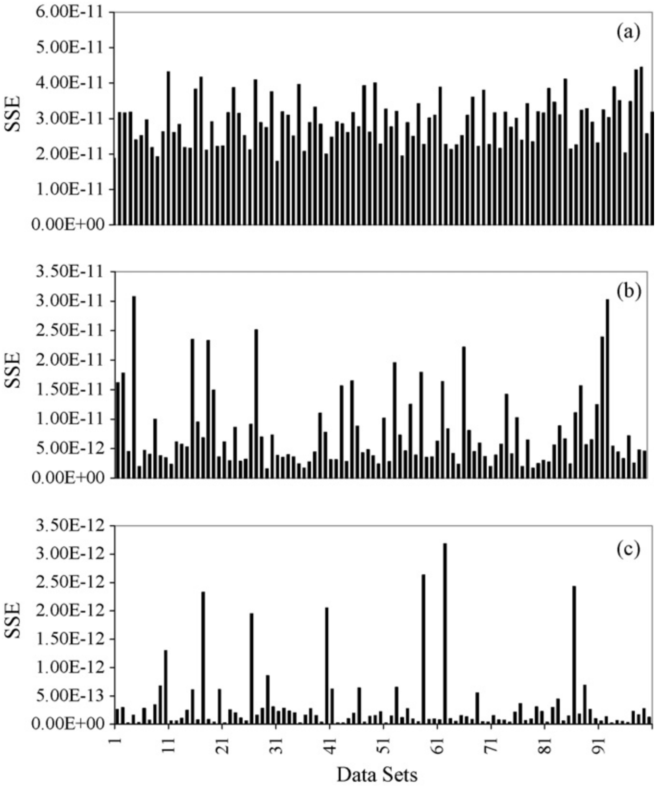

Fig. 3. Results of Monte Carlo simulation at 252.5 °C: (a) $0.00001<K_{\mathrm{BT}}<0.001$, (b) $0.01<K_{\mathrm{BT}}<10$ and (c) $10<K_{\mathrm{BT}}<100$.

Then, a new range of k values is specified, for instance, $0.01<k<10$, and another hundred of random iterations is done. The results are shown in Fig. 2b. Again, the lowest values of the SSE are found at low k values. This process is repeated and Fig. 2c presents the results for $0.00001<k<0.001$. For this latter case very low values of SSE were found and hence, the order of magnitude of k is about 1×10^{-5}. The same procedure was followed for the other two parameters and their orders of magnitude were: $K_{\mathrm{H_2S}}$: 10; K_{BT}: 10. Fig. 3 shows the results for the case of K_{BT}. For the other temperatures corresponding to different model with four kinetic parameters (Eq. (5)), different orders of magnitude were found. These values can be used for initialization of parameters.

3.3. Results of nonlinear estimation

Once the order of magnitude of the different parameters has been established, they can be used as initial guess for the nonlinear parameter optimization. For this purpose Marquardt method [11] was employed.

Fig. 4 shows the corresponding iterative process. It is seen that the objective function really started at low values, which is obviously due to the correct initial guess of parameters determined by Monte Carlo method. The optimization process required about 160 iterations and parameter values seem to be the optimal.

The final results of calculated parameters are shown in Table 4, in which a comparison with those reported by Kilanowski and Gates [14] is presented. Most of the parameter values are equal or quite similar to the reported ones. The highest differences, although not really high, in both reported

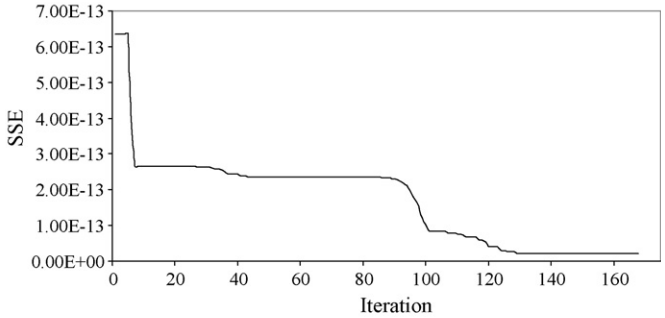

Fig. 4. Iterative process for minimization of the objective function at 252.5 °C.

Table 4
Comparison of reported [14] and calculated kinetic parameters

Temperature (°C)	Parameter	Reported values [14]	Calculated values	Optimized values
252.5	k^n	3.40×10^{-5}	3.3346×10^{-5}	3.3346×10^{-5}
	K_{BT}	3.95×10^{1}	3.9512×10^{1}	3.9512×10^{1}
	K_{H_2S}	1.20×10^{1}	1.1914×10^{1}	1.13184×10^{1}
302.0	k^n	2.36×10^{-4}	2.0197×10^{-4}	
	K_{H_2}	1.79×10^{-1}	1.5684×10^{-1}	
	K_{BT}	2.03×10^{2}	1.7640×10^{2}	
	K_{H_2S}	1.57×10^{2}	1.3699×10^{2}	
332.5	k^n	2.83×10^{-4}	2.8860×10^{-4}	
	K_{H_2}	6.54×10^{-2}	6.3078×10^{-2}	
	K_{BT}	8.71×10^{1}	8.8709×10^{1}	
	K_{H_2S}	8.73×10^{1}	8.9922×10^{1}	

k^n (gmol/g$_{cat}$ s atm^2), K_{BT} (atm^{-1}), K_{H_2S} (atm^{-1}), K_{H_2} (atm^{-1}).

and calculated parameter values are observed at temperature of 302 °C.

3.4. Sensitivity analysis

Analysis of parameter sensitivity was practiced for k, K_{H_2S} and K_{BT} in the model at 252.5 °C (Eq. (4)), and for k, K_{H_2S}, K_{BT} and K_{H_2} in the model at 302 °C and 332.5 °C (Eq. (5)) by means of ±20% perturbations in the original parameter values determined by nonlinear regression and reported in the previous section. For each perturbation in each parameter, the objective function was evaluated and the results are presented in Figs. 5–7, for the models at 252.5, 302, and 332.5 °C, respectively.

From Figs. 6 and 7 it is clearly seen that the estimated parameters are the optimum since at 0% perturbation the SSE is the minimum, which is the condition to assure the correct values of parameters. Some parameters in these figures seem to give different minimum than the other parameters but the minimum is indeed the same since they are plotted in the secondary Y-axis with different scale. On the contrary, in Fig. 5 it is evident that only k and K_{BT} yield the same minimum at 0% perturbation while K_{H_2S} give another minimum at different perturbation.

From a graphic analysis of Fig. 5, the new value of K_{H_2S} can be obtained. To find it by graphic visualization, one can try a kind of “zoom” in the perturbation percentage, say ±10% instead of ±20% just to expand the scale. The results with this new perturbation range are presented in Fig. 8. As can be seen the minimum of the objective function is achieved at −5% perturbation of the original value of K_{H_2S}. The optimized value of this parameter is shown in the last column of Table 4.

With the optimized values of kinetic parameters sensitivity analysis is performed again and the results are shown in Fig. 9.

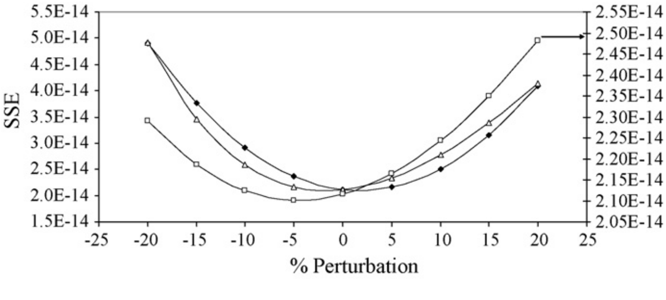

Fig. 5. Sensitivity analysis of calculated parameters for the model at 252.5 °C. (♦) k, (△) K_{BT}, (□) K_{H_2S}.

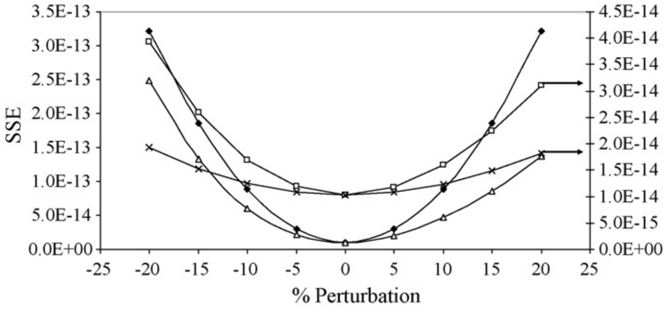

Fig. 6. Sensitivity analysis of calculated parameters for the model at 302 °C. (♦) k, (△) K_{BT}, (x) K_{H_2}, (□) K_{H_2S}.

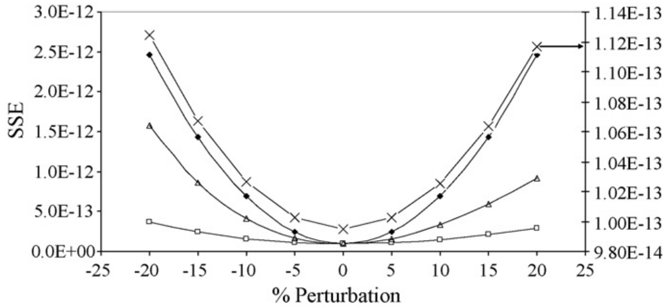

Fig. 7. Sensitivity analysis of calculated parameters for the model at 332.5 °C. (♦) k, (△) K_{BT}, (x) K_{H_2} (□) K_{H_2S}.

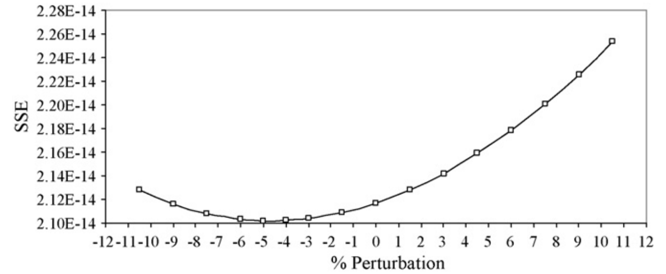

Fig. 8. Sensitivity analysis of parameter K_{H_2S} with ±10% perturbation for the model at 252.5 °C.

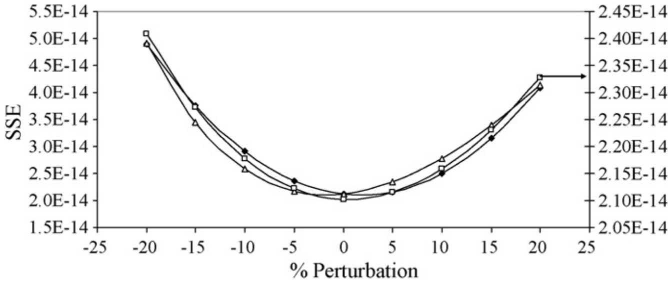

Fig. 9. New Sensitivity analysis of optimized parameters for the model at 252.5 °C. (♦) k, (△) K_{BT}, (x) K_{H_2}, (□) K_{H_2S}.

Now, the three parameters gave the same minimum at 0% perturbation, and hence, the global minimum is guaranteed and the optimization process is successfully finished.

It is then clear that by sensitivity analysis one can find those parameters providing different minima than others at different perturbation values, as was demonstrated in Figs. 5 and 8. In such cases a graphic examination of the sensitivity analysis curve must be done and with the corresponding perturbation values giving the different minima new values of those parameters can be re-calculated.

Table 5 summarizes the values of the objective function given by the sum of square errors determined with the reported kinetic parameters [14], and with the calculated and optimized values obtained in this work. It is observed that in general in all cases the parameter values determined in this work have given the lowest SSE. This confirms that the proposed methodology yields the best set of parameters which guaranties the global minimum of the objective function.

3.5. Analysis of residuals

Fig. 10 shows the residual analysis applied in each of the heterogeneous kinetic models at 252.5, 302 and 332.5 °C. Fig. 10a presents the results for the first set of calculated parameters, and Fig. 10b the results for the optimized values of parameters, in which only the corresponding values at 252.5 °C are shown. In both cases regular distribution of residuals without patterns is observed, indicating the adequacy of the estimated parameters. However, as was demonstrated before the set of parameters at 252.5 °C presented in Fig. 10b gives slightly lower residuals than that of Fig. 10a (average absolute residuals of 2.586×10^{-8} versus 2.646×10^{-8}, respectively). These results support the fact that residual analysis, although being a good method for checking the quality of the fit, cannot guarantee that the estimated parameters give the global minimum of the objective function.

Table 5
SSE determined with reported, [14] calculated and optimized kinetic parameters

Temperature (°C)	Set of kinetic parameters		
	Reported values[a]	Calculated values	Optimized values
252.5	2.100×10^{-14}	2.117×10^{-14}	2.100×10^{-14}
302	1.039×10^{-14}	1.034×10^{-14}	1.034×10^{-14}
332.5	9.990×10^{-14}	9.947×10^{-14}	9.947×10^{-14}

[a] The authors reported different values [14], but they were re-calculated in this work.

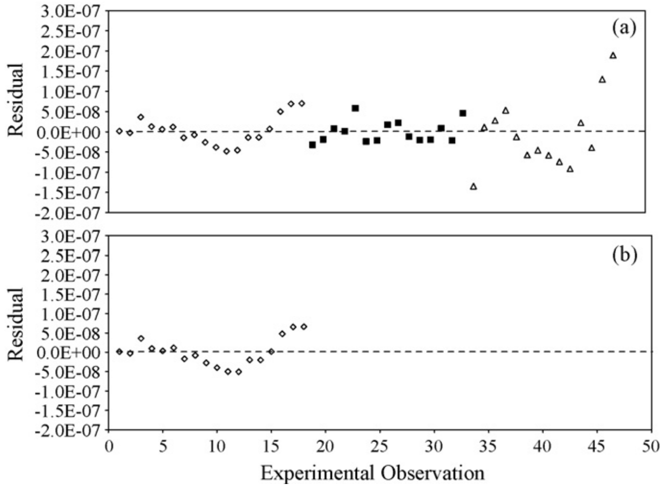

Fig. 10. Residual analysis for the model at (◇) 252.5 °C, (■) 302 °C, (△) 332.5 °C. (a) For the first set of calculated parameters and (b) for optimized values of parameters.

4. Conclusions

A step-by-step methodology is proposed in this work for determining parameters in heterogeneous kinetic models. The main advantage of the proposed method is the achievement of the optimal values of kinetic parameters by assuring the minimization of the objective function to the global minimum and not to local minima.

Various approaches are considered in the methodology: initialization of parameters (analysis of orders of magnitude, Monte Carlo simulations), nonlinear parameter estimation, parameter sensitivity analysis, residual analysis, which if applied properly can guarantee the best set of parameters for a given model.

Parameter estimation with the case of study used in this work showed that the proposed methodology indeed assures the optimization of kinetic parameters values giving lower error than reported ones.

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