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Experimental errors in kinetic tests and its influence on the precision of estimated parameters. Part I—Analysis of first-order reactions

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ABSTRACT

The proper characterization of the experimental errors is essential for the correct evaluation of estimated model parameters, model fit and model predictions based on kinetic rate expressions. However, it is common to ignore the influence of experimental errors during kinetic studies due to difficulties to characterize how experimental errors depend on the reaction conditions. The behavior of experimental error depends on the specific features of the experimental system; however, in many cases the main sources of experimental errors are the unavoidable oscillations of the input variables. This work analyzes how the experimental errors affect kinetic studies based on catalytic tests when oscillations of the input variables are the main sources of uncertainties. The first part of this work assumes that the reaction rate can be described accurately as a first-order reaction in a PFR. Analytical expressions are derived for the variance of the reactant conversion in distinct scenarios and are used to analyze the quality of the obtained parameter estimates. It is shown here that the conversion variances can be described as functions of the measured conversion values, normally presenting a point of maximum for conversion values in the range of $0.6 < X < 1.0$ when observed experimental fluctuations are controlled by the fluctuations of the input variables. Constant conversion variances should be expected only when fluctuations are controlled by analytical conversion measurements. As a consequence, optimum parameter estimation may be performed either with differential or integral methods, depending on the behavior of the conversion variances.

1. Introduction

Kinetic expressions are useful tools for the evaluation, comparison and prediction of catalyst activity, allowing for the optimization of catalyst performance both in laboratory and industrial scales. The analysis of models and kinetic parameters may also help to clarify catalytic routes and understand reaction paths, as usually performed in kinetic studies [1,2].

In order to analyze catalyst performance and obtain kinetic parameters, differential methods have normally been employed. The main reason for the widespread usage of this kind of kinetic analysis is the simple calculation of reaction rates (which does not require numerical integration of balance equations), based on the assumption of negligible variation of concentration (or partial pressure) of the reactants. In these systems, the conversion is kept at low values (<20%), so that it is possible to assume that the kinetic rate is constant along the reactor length [2,3].

On the other hand, the use of differential methods may not be appropriate for kinetic studies. First, the conditions required to keep the conversion at low values may impose limits on the experimental ranges of operation variables, such as volumetric flow, partial pressure of reactants and reaction temperature in order to keep the conversion at low values. Second, obtained conversion values may be very similar to each other, making the statistical discrimination of available data very difficult, when the experimental errors are taken into consideration. These restricted conditions are not imposed for the use of integral methods, since they can be used at any conversion level.

Conversely, statistical experimental designs have been proposed to allow for adequate variation of operation variables and process responses, allowing for more precise estimation of model parameters and identification of experimental effects. In this context the use of differential methods in order to avoid the numerical integration of balance equations may not be justified, as sophisticated numerical techniques and computer software are available nowadays for the immediate integration of mass and energy balances. Therefore, it is not necessary to assume that operation conditions are constant along the reactor volume and/or during the experimental run in order to analyze obtained kinetic data.

The estimation of model parameters is usually performed through minimization of a metric function that represents the distance between the experimental and the calculated response

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Nomenclature

$\mathbf{B}$	sensitivity matrix
b_{ij}	ij-element of sensitivity matrix
C	constant value defined in Eq. (12)
S	objective function
T	temperature
v	volumetric flow rate
$\mathbf{V}_{\boldsymbol{\theta}}$	covariance matrix of parameter estimates
$\mathbf{V}_{\mathbf{y}}$	experimental covariance matrix
W	catalyst mass
X	conversion
$\mathbf{x}$	inlet variables
y	outlet or response variables
α	packing quality of the catalyst bed
$\boldsymbol{\theta}$	model parameter
σ_{XA}^2	variance of analytical measurement of variance
σ_W^2	variance of catalyst mass
σ_X^2	variance of conversion
σ_y^2	variance of outlet variable
σ_θ^2	variance of parameter estimate
σ_T^2	variance of temperature
σ_v^2	variance of volumetric flow rate

values. Most kinetic studies do not take into account the variance of the measured values and, in this case, statistical tests cannot be applied properly to evaluate the model adequacy and the quality of model parameters and of the model fit [4].

A more fundamental procedure is based on the assumption that the experimental errors follow the normal distribution, the model is perfect and experiments are well done. In this case, it can be shown that the parameter values can be obtained through the minimization of the likelihood function, defined as [5,6]:

$$S = \sum_i \frac{(y_i^e - y_i^c(\mathbf{x}, \theta))^2}{\sigma_{yi}^2} \tag{1}$$

where the index i indicates the experimental point; y_i^e represents the values of experimental values of process responses; y_i^c represents the calculated values of process responses, calculated as a function of inlet design variables ($\mathbf{x}$) and model parameters ($\boldsymbol{\theta}$); and σ_{yi}^2 is the variance of process response measurements. (Rigorously, the determination of the probability distribution of a particular measurement can be obtained only through extensive replications. However, most times this is not feasible, due to time and cost constraints. The normal distribution is often assumed because it allows for close representation of many measurement distributions and because the mathematical treatment of the data is simple, as only the mean value and the variance are needed. The proposed analysis can be extended to non-normal problems with the help of more involving numerical schemes [5,6]; however, this is beyond the scope of the present manuscript.)

In Eq. (1), each difference between experimental and model response values is weighted by the respective experimental error. So, experimental points that are subject to large experimental uncertainties do not influence the objective function significantly. As a consequence, the distance between model responses and experimental data tends to be smaller when the experimental variances are small. Therefore, the correct characterization of experimental error is a fundamental issue during estimation of model parameters and analysis of experimental data. This may be very important because the precision of experimental measurements is transferred to the precision of kinetic parameters, which in turn are transferred to precision of output model predictions.

Usually, the experimental error is completely ignored in kinetic problems. For this reason, estimation of model parameters and model building are carried out with the help of the well-known least squares function [7–10]. The underlying hypothesis that justifies the use of the least squares function is that the experimental error is the same for all measurements. In some cases, the variance in Eq. (1) is considered equal or an arbitrary fraction of the measured variable [11,12].

The resistance that many offer for proper characterization of experimental errors is understandable. As a matter of fact, as already said the correct characterization of experimental errors usually demands a large number of replicates, which may be many times unfeasible, due to existence of time and cost constraints. Therefore, techniques that allow for the simultaneous evaluation of experimental errors and minimization of the experimental efforts are welcome [4,5,13–16].

The parameter uncertainties can be represented in terms of the covariance matrix of parameter uncertainties ($\mathbf{V}_{\boldsymbol{\theta}}$), defined as [4,5]:

$$\mathbf{V}_\theta = (\mathrm{B}^T \cdot \mathrm{V}_y^{-1} \cdot \mathrm{B})^{-1} \tag{2}$$

where $\mathbf{V}_y$ is the covariance matrix of experimental process response measurements and $\mathbf{B}$ is the sensitivity matrix, defined as:

$$\mathrm{B} = [b_{ij}] = \left[\frac{\partial y_j}{\partial \theta_i}\right] \tag{3}$$

In order to obtain precise parameter values, a specified metric of the matrix $\mathbf{V}_{\boldsymbol{\theta}}$ must be minimized, which can be used for the design of the experimental conditions. For a first-order reaction ($A \rightarrow B$, $r_A = -\boldsymbol{\theta} \cdot P_A$) where the output process response is the conversion (X) of reactant A, the precision of parameter $\boldsymbol{\theta}$ after NE experiments can be obtained as:

$$\frac{1}{\sigma_\theta^2} = \sum_{i=1}^{NE} \frac{(\partial X_i / \partial \theta)^2}{\sigma_{X_i}^2} \tag{4}$$

For one to use Eq. (4) in order to characterize the precision of the kinetic parameter and of the calculated model responses, it is necessary first to characterize the experimental error of experimental data. However, $\sigma_{X_i}^2$ may depend on specific features of the analyzed catalyst system, which may involve the precision of reactant feed rates, the control of reactor conditions, the precision and accuracy of off-line laboratory analyses, etc. The technical literature has largely overlooked this issue.

It seems clear that experimental errors are not necessarily constant throughout the experimental range. For example, Pereira et al. [17] studied the gibbsite dissolution in the presence of NaOH and concluded (based on an extensive experimental plan), that the conversion variances depended on the measured conversion values. The authors fitted an empirical model to available data to describe the conversion variance as a function of the conversion.

Larentis et al. [18] investigated the sources of error in reaction systems involving gaseous species and on-line chromatographic analyses. The proposed error analysis allowed for the identification of the predominant reactions that were occurring in different experimental ranges. Besides, it was shown that the main sources of error were probably associated with the catalyst activity, which can be affected by the catalyst itself, the preparation of the catalyst bed or the operational conditions of the reactor.

Gutierrez and Danielson [19] analyzed the error structure of dynamic enzymatic assays when the initial enzyme and substrate concentrations are subject to uncertainties. They showed that the variance of the substrate conversion presents a heteroscedastic behavior in these cases, reaching a maximum value around 60–80%, which could be described with the help of a hybrid empirical-phenomenological model.

Based on previous remarks, it may be concluded that the proper characterization of experimental errors can be extremely useful for those who are working in the field of chemical kinetics and catalysis. Besides, it can also be said that experimental errors are not necessarily constant in the experimental region for better understanding of the reaction system, as shown experimentally and explored theoretically. For these reasons, model equations are proposed in the present work to represent how experimental variances depend on reaction conditions in typical catalyst tests. The main pursued objective is the development of a theoretical framework that may allow for simultaneous characterization of variances and minimization of the number of replicate runs. In this manner, more involving and rigorous statistical analyses of available data may become possible, even when the number of replicates is small.

It is assumed here that a first-order reaction is carried out in a plug flow reactor at isothermal conditions. It is also assumed that diffusion constraints are absent. These constraints should not be overemphasized because catalyst tests are normally performed isothermically in plug flow reactors and because first-order reaction rate expressions are frequently used for model building and kinetic analysis. Initially, first-order kinetics is used frequently as a first model building stage. Second, first-order kinetics may be regarded as a local linearization of more involving kinetic mechanisms. Third, the main objective of the present paper is showing that experimental errors may depend quite considerably on the operation conditions, which has been largely overlooked in the field of kinetics and catalysis. In order to illustrate this point, complex kinetic schemes are not necessary, as shown in the present manuscript. In spite of the previous remarks, it is important to say that the analysis of more complex reaction systems can also be performed with the help of the proposed differential analysis.

It is shown here that the conversion variances can be described as functions of the measured conversion values, presenting a point of maximum conversion variance in the conversion range of $0.6 < X < 1.0$ when observed experimental fluctuations are controlled by the fluctuations of the input variables. As presented in the following sections, constant conversion variances should be expected only when fluctuations are controlled by errors in the analytical measurement of the outlet variables, as the conversion. As a consequence, optimum parameter estimation may be performed either with differential or integral methods, depending on the behavior of the conversion variances.

2. Conversion variance for a first-order reaction

Let us assume that a catalytic system is designed to operate isothermally. At the desired reaction temperature (T_D), volumetric flow rate (v_D) and catalyst bed mass (W_D), the expected conversion is X_D. However, in this hypothetical system, the experimental design variables are subject to fluctuations, so that the real temperature (T), volumetric flow rate (v) and mass of catalyst (W) are different from the desired design values, leading to a different conversion (X).

Expressing the conversion as a function of the design variables in terms of a Taylor series truncated after the first term:

$$X \approx X_D + \left[\left(\frac{\partial X}{\partial T}\right)\bigg|_{T=T_D}\right](T-T_D) + \left[\left(\frac{\partial X}{\partial v}\right)\bigg|_{v=v_D}\right](v-v_D) + \left[\left(\frac{\partial X}{\partial W}\right)\bigg|_{W=W_D}\right](W-W_D) \tag{5}$$

or

$$\Delta X \approx \left[\left(\frac{\partial X}{\partial T}\right)\bigg|_{T=T_D}\right]\Delta T + \left[\left(\frac{\partial X}{\partial v}\right)\bigg|_{v=v_D}\right]\Delta v + \left[\left(\frac{\partial X}{\partial W}\right)\bigg|_{W=W_D}\right]\Delta W \tag{6}$$

Squaring and averaging both sides of Eq. (6), in order to obtain the conversion variance (≈ is replaced by =, observing that the expected value of Δz^2 is the variance σ_z^2, where z is any variable):

$$\sigma_X^2 = \left\{\left[\left(\frac{\partial X}{\partial T}\right)\bigg|_{T=T_D}\right]\sigma_T + \left[\left(\frac{\partial X}{\partial v}\right)\bigg|_{v=v_D}\right]\sigma_v + \left[\left(\frac{\partial X}{\partial W}\right)\bigg|_{W=W_D}\right]\sigma_W\right\}^2 \tag{7}$$

Assuming that random fluctuations of the design variables are not correlated to each other:

$$\sigma_X^2 = \left[\left(\frac{\partial X}{\partial T}\right)\bigg|_{T=T_D}\right]^2\sigma_T^2 + \left[\left(\frac{\partial X}{\partial v}\right)\bigg|_{v=v_D}\right]^2\sigma_v^2 + \left[\left(\frac{\partial X}{\partial W}\right)\bigg|_{W=W_D}\right]^2\sigma_W^2 \tag{8}$$

Eq. (8) is frequently used in statistics to perform robust processes or product design [20].

For a first-order reaction, the conversion can be written as:

$$X = 1 - \exp\left(-\theta_0 \cdot e^{-(\theta_1/T)}\frac{W}{v}\right) \tag{9}$$

Therefore,

$$\frac{\partial X}{\partial T} = \underbrace{-\exp\left(-\theta_0 \cdot e^{-(\theta_1/T)} \cdot \frac{W}{v}\right)}_{1-X}\underbrace{\theta_0 \cdot e^{-(\theta_1/T)} \cdot \frac{W}{v}}_{\ln(1-X)}\frac{\theta_1}{T^2} \tag{10a}$$

$$\frac{\partial X}{\partial v} = \underbrace{-\exp\left(-\theta_0 \cdot e^{-(\theta_1/T)} \cdot \frac{W}{v}\right)}_{(1-X)}\underbrace{-\theta_0 \cdot e^{-(\theta_1/T)} \cdot \frac{W}{v}}_{\ln(1-X)}\frac{1}{v} \tag{10b}$$

$$\frac{\partial X}{\partial W} = \underbrace{-\exp\left(-\theta_0 \cdot e^{-(\theta_1/T)} \cdot \frac{W}{v}\right)}_{(1-X)}\underbrace{-\theta_0 \cdot e^{-(\theta_1/T)} \cdot \frac{W}{v}}_{\ln(1-X)}\frac{1}{W} \tag{10c}$$

Inserting Eqs. (10) in Eq. (8) and rearranging:

$$\sigma_X^2 = [(1-X)\ln(1-X)]^2 \cdot \left\{\frac{\theta_1^2}{T^4}\sigma_T^2 + \frac{\sigma_v^2}{v^2} + \frac{\sigma_W^2}{W^2}\right\} \tag{11a}$$

If the evaluation of X is also subject to a measurement error with variance σ_{XA}^2, then Eq. (11a) should be written as:

$$\sigma_X^2 = [(1-X)\ln(1-X)]^2 \cdot \left\{\frac{\theta_1^2}{T^4}\sigma_T^2 + \frac{\sigma_v^2}{v^2} + \frac{\sigma_W^2}{W^2}\right\} + \sigma_{XA}^2 \tag{11b}$$

Now it is necessary to evaluate the terms involving the design variables and its variances. If the analyzed experimental range is not very large and/or the relative error measurements are constant, the terms inside the brackets may be regarded as constant and represented by C. In this case, Eq. (11) can be written as:

$$\sigma_X^2 = C \cdot [(1-X)\ln(1-X)]^2 \tag{12a}$$

$$\sigma_X^2 = C \cdot [(1-X)\ln(1-X)]^2 + \sigma_{XA}^2 \tag{12b}$$

Eq. (12) presents interesting characteristics, as shown in Fig. 1, for an arbitrary C value. In Fig. 1A, the conversion variance presents a maximum value at X equal to 0.63, with inflection points at X equal

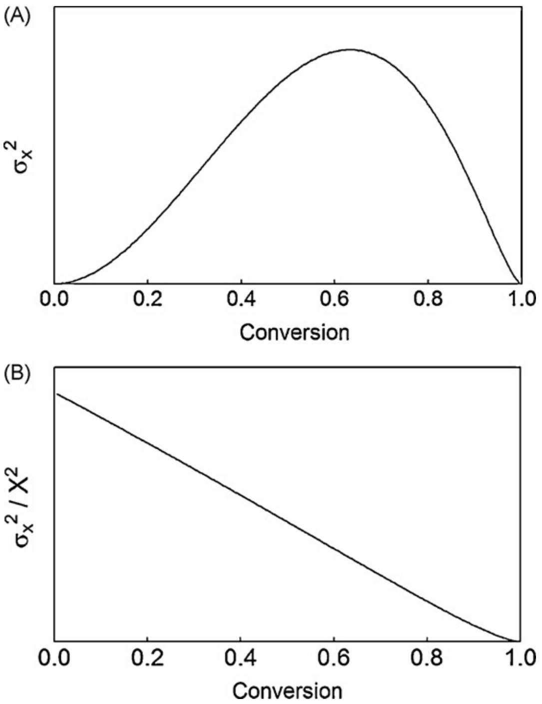

Fig. 1. Variance of the conversion (A) and relative conversion variance (B) as a function of conversion for Eq. (11).

to 0.32 and 0.93. When conversion is equal to zero, conversion variance is also equal to zero because the reactant concentration does not change and the reactor output is not subject to process fluctuations. As the conversion increases, the conversion variance also increases, since variations of the reaction conditions perturb the measured conversion values and the influence of process fluctuations is larger when reaction rates are high and the magnitude of conversion values increases. However, the continuous increase of conversion leads to appearance of a point of maximum conversion variance. After this point of maximum, the variance of conversion decreases, as reaction rates at high conversion values become lower and perturbations of the operating conditions cause less significant effects on the observed reaction rates. If the relative conversion variances are considered (that is, the conversion variance divided by squared conversion values), as presented in Fig. 1B, one can observe that the relative conversion variance decreases almost linearly with conversion, given the higher reaction rates observed at lower conversions.

It must be noted that Gutierrez and Danielson [19,21] developed an equation for the variance of substrate conversion in dynamic enzymatic assays that is similar to Eq. (12). This clearly shows that Eq. (12) may find application in distinct experimental systems.

Eq. (12) can be very useful because it describes the conversion variance in terms of the measured conversion values. Therefore, if replicates are available at a certain experimental condition, it is possible to determine the constant C:

$$\sigma_X^2 = (\sigma_{X0}^2 - \sigma_{XA}^2)\cdot\frac{[(1-X)\ln(1-X)]^2}{[(1-X_0)\ln(1-X_0)]^2} + \sigma_{XA}^2 \tag{13}$$

where σ_{X0}^2 represents the available conversion variance and X_0 represents the average conversion obtained from available replicates.

Obviously, the characterization of the variance in a single point may lead to inaccurate representation of conversion variances in the whole experimental range. Nevertheless, it seems much more reasonable to use Eq. (13) for more fundamental data analysis than to ignore the effect of fluctuations of the design variables on the conversion variances.

It must be pointed that the parameter C will not be constant if the experimental region of design variables is large and variances of the design variables are not proportional to measured values. Therefore, one must consider that Eq. (13) can constitute a useful approximation of the real variance behavior.

3. Optimum estimation of the kinetic parameter

Temperature effects are neglected in the following paragraphs. Therefore, the well-known Arrhenius equation is not used to represent the temperature dependence of the kinetic rate constant. This assumption will be relaxed in the following sections. In this case, using Eq. (4) to obtain $1/\sigma_\theta^2$, it is possible to write:

$$\frac{1}{\sigma_\theta^2} = \frac{(\partial X/\partial\theta)^2}{\sigma_X^2} \tag{14}$$

The partial derivative of conversion in respect to the kinetic constant is:

$$\frac{\partial X}{\partial \theta} = -\underbrace{\exp\left(-\theta\cdot\frac{W}{v}\right)}_{(1-X)}\left[\underbrace{-\theta\cdot\frac{W}{v}}_{\ln(1-X)}\frac{1}{\theta}\right] \tag{15}$$

This can also be written in terms of the conversion, as:

$$\frac{\theta^2}{\sigma_\theta^2} = \frac{(1-X)^2\ln^2(1-X)}{\sigma_X^2} \tag{16}$$

The most precise estimation of parameter $\boldsymbol{\theta}$ can be achieved when the variance of the model parameter has a minimum value. This is equivalent to maximizing the right-hand side of Eq. (16). In order to do that, three cases are considered below: (i) constant conversion variance (least squares function), meaning that uncertainties are controlled by off-line laboratory analyses; (ii) conversion variance described by Eq. ((12)–(13)), meaning that uncertainties are controlled by the constant precision of the input variables; and (iii) conversion variance described by Eq. (11), meaning that uncertainties are controlled by the varying precision of the input variables.

3.1. Constant conversion variance

Based on Eq. (11), the conversion variance is constant when uncertainties are controlled by off-line laboratory analyses. In this case, maximizing Eq. (16) is equivalent to maximizing the following equation:

$$\max\frac{1}{\sigma_\theta^2} = \max\,(1-X)^2\ln^2(1-X) \tag{17}$$

which has a maximum placed at the value for X equal to 0.63. Based on this result, it may be concluded that, when the experimental error is constant (and the analytical errors are predominant), it is preferable to use integral methods for model building and precise and accurate parameter estimation. This may be regarded as a very important conclusion, given the widespread usage of differential kinetic analysis in the field of catalysis.

However, according to Eq. (12), this is the point where the conversion variance is maximum (when it is assumed that the conversion variance is not constant). This constitutes a very important result, because this means that the experimental optimum design (when the conversion variance is constant) indicates that the optimal experiment is placed at the region where the conversion variance attains its highest value (when the conversion variance is not constant). Therefore, if one assumes that conversion variances are constant and the assumption is not correct, experimental design will erroneously recommend the experimental region where measurement errors attain the largest values. This clearly illustrates the importance of taking into account the proper interpretation of experimental errors in order to avoid very bad data analysis and experimental design.

3.2. *Conversion variance described by Eq. (12)*

If the conversion variance is described by Eq. (12), meaning that uncertainties are controlled by the constant precision of the input variables, the error of parameter estimate can be determined as:

$$\frac{\theta^2}{\sigma_\theta^2}=\frac{(1-X)^2\ln^2(1-X)}{(1-X)^2\ln^2(1-X)\cdot C+\sigma_{XA}^2}=\frac{1}{C+(\sigma_{XA}^2/(1-X)^2\ln^2(1-X))} \tag{18}$$

If the analytical conversion variance σ_{XA}^2 is neglected, then the parameter variance does not depend explicitly on the experimental conditions (although it depends on the obtained conversion, because it is a function of $\boldsymbol{\theta}$, which is obtained as a function of the observed conversion), which is very surprising! However, if σ_{XA}^2 is considered, then Eq. (12) must be maximized in order to minimize the parameter variance. Once more, this means that the optimum experimental conditions are the ones that lead to conversion values around 0–63%, when the reaction follows the first-order kinetics. As observed in the previous case, this clearly shows that the kinetic tests performed through differential methods may not be adequate for kinetic analysis, as the parameter variance approaches its maximum value when conversion approaches zero! Therefore, it may be concluded once more that it is preferable to use integral methods for model building and precise parameter estimation. Again, this may also be regarded as a very important conclusion, given the widespread usage of differential kinetic analysis in the field of catalysis.

3.3. *Conversion variance described by Eq. (11)*

If the conversion variance is described by Eq. (11), meaning that uncertainties are controlled by the varying precision of the input variables, the parameter variance can be written as:

$$\frac{\theta^2}{\sigma_\theta^2}=\frac{1}{\left\{\frac{\theta_1{}^2}{T^4}\sigma_T^2+\frac{\sigma_v^2}{v^2}+\frac{\sigma_W^2}{W^2}\right\}+\frac{\sigma_{XA}^2}{(1-X)^2\ln^2(1-X)}} \tag{19}$$

It is necessary to perform the maximization of Eq. (19) in order to obtain the best experimental conditions for estimating the model parameter. If the variances of input variables are constant, the right-hand side of Eq. (19) presents a monotonic behavior with respect to volumetric flow rate and mass of catalyst. The dependence of Eq. (19) with respect to temperature is more complex because the model parameter certainly depends on the reaction temperature. In order to show the main trends, it is preferable to evaluate the variance behavior when the fluctuations are controlled by a single input variable.

3.3.1. *The flow rate effect is predominant*

Considering that the effects of the temperature and catalyst mass in the conversion variance are negligible and only the effect of the flow rate is important, from Eq. (11), the conversion variance can be written as:

$$\sigma_X^2=[(1-X)\ln(1-X)]^2\cdot\left\{\frac{\sigma_v^2}{v^2}\right\}+\sigma_{XA}^2 \tag{20}$$

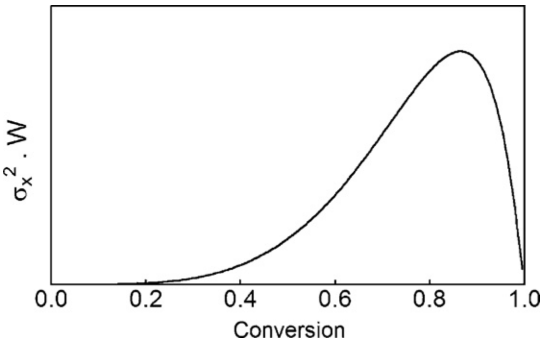

Fig. 2. $\sigma_X^2\cdot W$ as a function of conversion for Eq. (22).

The volumetric flow rate can be expressed in terms of conversion as:

$$v=-\frac{\theta\cdot W}{\ln(1-X)} \tag{21}$$

Inserting Eq. (21) into Eq. (20):

$$\sigma_X^2\cdot W^2=\frac{\sigma_v^2}{\theta^2}\cdot(1-X)^2\ln^4(1-X)+\sigma_{XA}^2\cdot W^2 \tag{22}$$

If the analytical error can be neglected, the conversion variance can be evaluated by the expression $[(1-X)^2\ln^4(1-X)]$, presented in Fig. 2 as a function of X. Considering the variance of the volumetric flow constant, the right-hand side of Eq. (22) presents a maximum at X equal to 0.86. Again, for low and high values of conversion, the conversion variance tends to be lower than for intermediate values of conversion.

In order to determine the optimal experimental run for precise parameter estimation, the conversion variance defined in Eq. (22) must be inserted into Eq. (16) (or one can simplify Eq. (19) by assuming that the effect of the flow rate is predominant) resulting in:

$$\frac{\theta^2}{\sigma_\theta^2}=\frac{v^2}{\sigma_v^2} \tag{23}$$

If the variance of the volumetric flow rate is constant, the parameter $\boldsymbol{\theta}$ is estimated with more precision when the volumetric flow is maximum. Eq. (23) indicates that $\boldsymbol{\theta}$ is estimated with more precision when the conversion is lower. Again, this may be regarded as a very important result, as it indicates that the correct evaluation of the experimental error changes completely the determination of the best region for precise parameter estimation. Therefore, when the variance of the feed flow rate controls the precision of output responses, the use of differential methods in the kinetic analysis may be considered, since at high volumetric flow the conversion is usually low and the reaction rate can be regarded as constant along the reactor length.

3.3.2. *The temperature effect is predominant*

This may be the case of highly endo/exothermic reactions or systems where the temperature control is difficult. Considering that only the deviations in the temperature are important, from Eq. (11), the conversion variance can be written as:

$$\sigma_X^2=[(1-X)\ln(1-X)]^2\left[\frac{\theta_1^2}{T^4}\sigma_T^2\right] \tag{24}$$

The conversion variance cannot be expressed as a function of conversion only, as it also depends on the flow rate and mass of catalyst. If reactor temperature is assumed to be constant, the behavior of the variance conversion is similar to the one illustrated in Fig. 1. In this case, the conversion variance is higher for lower tempera-

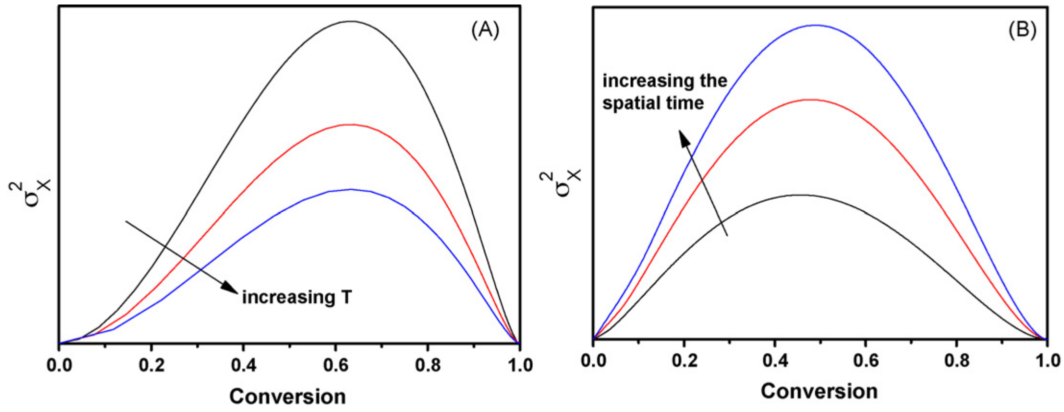

Fig. 3. Variance of the conversion a function of conversion: (A) for three temperatures and several spatial times; and (B) for three spatial times and several temperatures.

tures, as clearly seen in Eq. (24). In order to illustrate this effect, let us assume that:

$$\theta = 100 \cdot \exp\left(-\frac{3000}{T}\right) \tag{25}$$

Based on Eq. (25), the conversion value and the respective conversion variance were calculated for distinct temperatures and residence times. The obtained results are presented in Fig. 3. When temperature is varied, the behavior of the conversion variance may be very complex and depends on the kinetic parameters and the spatial times. Despite that, in all cases intermediate conversion value leads to larger conversion variances.

In order to determine the optimal conditions for precise parameter estimation, Eq. (19) can be written as:

$$\frac{\theta^2}{\sigma^2_\theta} = \frac{1}{\left\{\left(\frac{\theta_1^2}{T^4}\right)\sigma^2_T\right\}} \tag{26}$$

Maximization of Eq. (26) can be achieved at high temperatures, meaning that when the error is controlled by temperature effects, experiments should be performed at the maximum allowable temperature values in order to minimize the variance of the kinetic parameter. One must observe that high temperature conditions also lead to lower values of the conversion variance, as shown in Fig. 3. This is very interesting, since when the conversion variance is not assumed constant and the temperature effect in the experimental error is predominant, the designed experiments must be performed at experimental conditions where conversion variance has lower values. One must observe that when conversion variance was considered constant (Section 3.1) the experimental condition that minimizes the parameter estimate variance was the same where conversion variance reaches a maximum value. Once more, this shows the importance of considering the real behavior of the conversion variance, instead of using the much simpler assumption of constant conversion variance during data analysis.

As it becomes clear that the precision of estimated parameters depends not only on the experimental precision, but also on the selected experimental conditions. When the error is controlled by temperature effects, it can be concluded that experiments should be performed at the maximum allowable temperature values.

3.3.3. *The catalyst mass effect is predominant*

Considering now that the fluctuations in the catalyst mass are predominant, Eq. (19) can be expressed as:

$$\frac{1}{\sigma^2_\theta} = \frac{1}{\sigma^2_W}\frac{W^2}{\theta^2} \tag{27}$$

The variance of the catalyst mass is probably constant and related to the precision of the balance used to weigh the mass. According to Eq. (27), the optimal parameter estimation can be achieved when the mass of catalyst is equal to the maximum allowed value. Therefore, the parameter variance is smaller when the catalyst mass is larger. As one might already expect, the weighing of low catalyst masses may introduce large experimental errors in the analysis. As conversion tends to increase when the mass of catalyst increases, it can be said indirectly that the integral method is preferable when the conversion variance is controlled by fluctuations of the catalyst mass, since at high conversion values the differential method is not applicable.

3.4. *The packing effect*

It must be pointed out that packing of the catalyst bed does not depend directly on the design variables and should not be considered separately. The random packing of the catalyst bed may promote the occurrence of stagnant zones and short-cuts, resulting in different contact times between the fluid phase and the catalyst particles. For PFR reactors, this effect can be modeled in terms of two parallel reactors: one containing the catalyst and the other formed by void space, as illustrated in Fig. 4 [3]. According to the proposed model, α (which is quality of the packing of the catalyst bed) indicates the fraction of fluid that short-cuts the catalyst bed. α values can be estimated from Residence Time Distribution (RTD) experiments, using a trace step input [3].

The value of α may change from bed to bed, consequently leading to unavoidable fluctuation of the conversion. For a first-order

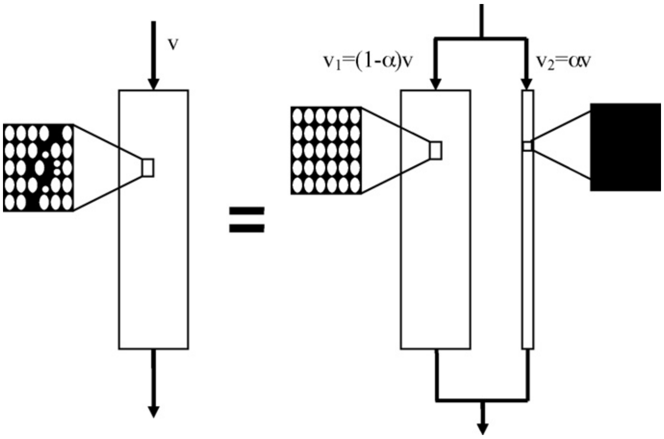

Fig. 4. Schematic representation of the real catalyst bed and the proposed bed model.

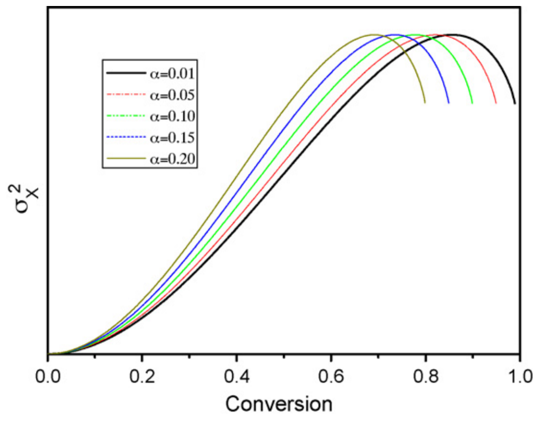

Fig. 5. Conversion variance as a function of conversion for several values of α in Eq. (32).

reaction, the conversion can be written as:

$$X = (1-\alpha)(1-\mathrm{e}^{-(\theta \cdot W/v(1-\alpha))}) \tag{28}$$

As performed previously, the conversion variance can be expressed as a function of characteristic fluctuations of α. So, the conversion variance can be written as:

$$\sigma_X^2 = \left(\frac{\partial X}{\partial \alpha}\right)^2 \sigma_\alpha^2 \tag{29}$$

As

$$\frac{\partial X}{\partial \alpha} = -1 + \exp\left(-k_0 \mathrm{e}^{-(E/RT)} \cdot \frac{W}{v_0(1-\alpha)}\right) + \exp\left(-k_0 \mathrm{e}^{-(E/RT)} \cdot \frac{W}{v_0(1-\alpha)}\right) k_0 \mathrm{e}^{-(E/RT)} \cdot \frac{W}{v_0(1-\alpha)} \tag{30}$$

Then

$$\frac{\partial X}{\partial \alpha} = 1 - \left(1 - \frac{X}{1-\alpha}\right) \cdot \left[1 + \ln\left(1 - \frac{X}{1-\alpha}\right)\right] \tag{31}$$

Therefore

$$\sigma_X^2 = \left\{\frac{X}{1-\alpha} - \left(1 - \frac{X}{1-\alpha}\right) \ln\left(1 - \frac{X}{1-\alpha}\right)\right\}^2 \sigma_\alpha^2 \tag{32}$$

This equation presents a maximum at:

$$X = \frac{1 + \mathrm{e}^2 + \alpha(1-\mathrm{e}^2)}{\mathrm{e}^2} \tag{33}$$

For good packing of the catalyst bed, α values must be close to zero. In this case, the maximum conversion variance would occur at X equal to 0.86. Fig. 5 shows the conversion variance as a function of conversion for several values of α. It can be observed that the conversion where the conversion variance attains it maximum value is shifted towards smaller values, as α increases. Besides, as α describes a short-cut fraction, conversion is limited to $1-\alpha$.

The best region for precise parameter estimation can be derived as shown previously. In this case, the parameter variance can be written as:

$$\frac{\theta^2}{\sigma_\theta^2} = \frac{(1-X)^2 \ln(1-X)^2}{\left\{\frac{X}{1-\alpha} - \left(1 - \frac{X}{1-\alpha}\right) \ln\left(1 - \frac{X}{1-\alpha}\right)\right\}^2} \frac{1}{\sigma_\alpha^2} \tag{34}$$

For a given temperature, the maximization of Eq. (34) leads to X equal to 0, as shown in Fig. 6 for different values of α. As it is probable that the quality of the catalyst bed may control the precision of the catalyst tests frequently, this may be regarded as a very important result. It indicates that reaction conditions should be selected in order to give small conversion values, allowing the increase in the precision of parameter estimates. It also can be observed that these conditions enable the use differential methods and may lead to more precise parameter estimation when errors are controlled by packing effects.

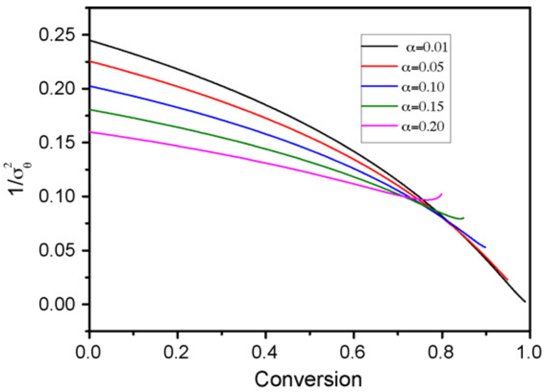

Fig. 6. Potential of estimation as a function of the conversion for several void fractions of the reactor.

3.5. Comparative analysis of the different scenarios

As shown in the previous paragraphs, the optimum experimental region for the estimation of model parameters and model building depends on the behavior of conversion variances. When the conversion variance is constant (and is controlled by analytical techniques), optimum determination of model parameters can be carried out with integral methods, as the lowest parameter variances are obtained for conversions values from 0 to 63%. Similar results can be obtained when the fluctuations induced by random variation of the design variables do not change considerably in the design region. Despite that, the maximum conversion variances are observed in the same experimental region, but are compensated by similar increase of conversion sensitivity to parameter estimation.

When the conversion variances are controlled by the design variables, then the scenario is not clear. For instance, experiments can be analyzed through differential methods if conversion variances are controlled by flow rate or packing fluctuations, or should be analyzed with integral methods if conversion variances are controlled by temperature of catalyst mass fluctuations.

4. Experimental validation of Eq. (13)

Based on experimental data reported in the literature [17,19], it can be assumed that Eq.(12) can be used to represent conversion variances in reaction systems described by kinetic rate expressions that are more complex than a first-order reaction. In order to evaluate the applicability of the present analysis in a real problem, experimental data reported in the literature were taken as an example. Pereira et al. [17] studied the dissolution of gibbsite in a solution of NaOH in a batch reactor. One can readily observe that similar analysis and equations can be obtained for batch reactors. The authors carried out replicates at different conditions and used an empirical expression to fit the conversion variance as a function of the measured conversion. The empirical equation was:

$$\sigma_X^2 = \exp(A + B \cdot X + C \cdot X^2) \tag{35}$$

where A, B and C are empirical fitting parameters.

Fig. 7 presents the experimental data reported by Pereira et al. [17] and a best fit obtained for Eq. (13). The conversion variance was described as a function of the X/X_{eq} ratio, where X_{eq} is the equilibrium conversion, equal to 94% at the analyzed experimental conditions. One must observe that maximum conversion variances occur at intermediate conversion values, as predicted by the pro-

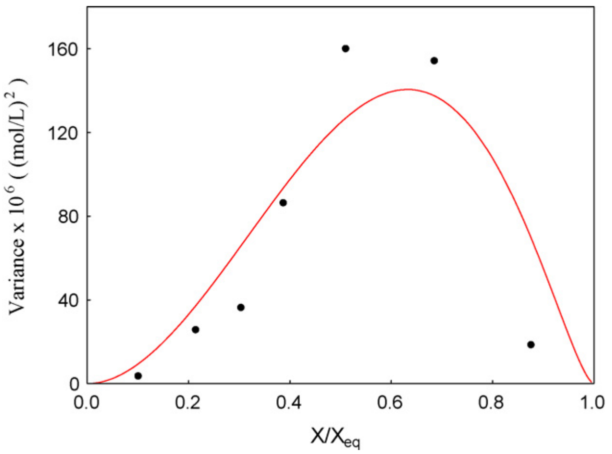

Fig. 7. Eq. (13) fitted to the data reported by Pereira et al. [17].

posed analysis. According to the authors, the kinetics of gibbsite dissolution could be described by a reversible expression written in terms of the external area of gibbsite particles and hydroxide anion concentration, which is not a simple first-order reaction. Even so, the adjustment of Eq. (13) to the available experimental data can be considered satisfactory, as it must be pointed out that the confidence intervals of the true variances obtained from triplicates are very large. The use of Eq. (13), even when obtained from a single experimental point, as described in Eq. (14), is certainly much more appropriate for sound evaluation of the experimental uncertainties than the usual assumption of constant conversion variance, as implicitly assumed when the procedure is used for the estimation of model parameters and data analysis. It is worthwhile mentioning that Pereira et al. [17] conclude that their kinetic evaluation depends on the assumed behavior of the experimental errors, thus reinforcing the analysis performed here.

5. Conclusions

This paper assessed the effects of experimental errors on the kinetic analysis of experimental data obtained during catalytic tests. Particular attention was given to conditions where the conversion variances were controlled by a single experimental design variable. Simple and useful expressions were derived to express how observed conversion variances depend on the experimental conditions, assuming first-order kinetics in a PFR.

It was shown that distinct optimum experimental designs for precise parameter estimation are obtained when distinct assumptions are made for the behavior of the experimental errors. This clearly indicates that proper characterization of experimental uncertainties may be of fundamental importance for rigorous statistical analysis of kinetic data. Particularly, it was shown that reaction temperatures, catalyst masses and spatial velocities should be made equal to the maximum allowed values. Besides, it was shown that conversion values should almost always lie in the range (0.50, 0.80), indicating that kinetic studies should almost always be performed through integral methods. Despite that, it was also shown that differential methods can be used when the errors are controlled by the quality of the catalyst packing or the oscillations of feed flow rates. Finally, it is important to emphasize that the use of integral methods is not restricted to experimental conditions that lead to small conversions and large relative conversion variances, as it happens when differential methods are used.

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