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Planning of experiments and kinetic analysis

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Abstract

In this paper we are taken into account the distinct phases necessary to build a kinetic model. In particular several mistakes, that can be made during such activity, are described and analyzed.

Keywords: Kinetic model; Experimental reactor; Parameter estimation; Statistical analysis

1. Introduction

One very important problem in chemical engineering is finding kinetic models for catalytic reactions. Frequently, the kinetic scheme includes several simultaneous reactions and therefore the kinetic model consists of several dependent variables. For the sake of simplicity, the case in which only one reaction occurs will be considered here as this naturally results in only one dependent variable. This limitation will not affect the observations which will be made. However, no restrictions are placed on the type of functional bond between the dependent variable and the independent variables.

The following phases are necessary to identify and analyze a kinetic model:

1. Selection of possible alternative kinetic models.
2. Selection of the experimental reactor.
3. Basic experimental design.
4. Determination of the model parameters.
5. Model discrimination.
6. Improvement of the parameter estimations.
7. Statistical analysis of the model.

An example will be considered to illustrate the errors which can be made during the search for and analysis of a kinetic model and the correct procedure which should be used.

The problem deals with the definition of a kinetic model for the toluene and hydrogen reaction toward benzene and methane

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4 \qquad (1)$$

as analyzed in Scott Fogler [1]. The principal points of this analysis are summarized in Table 1.

By analyzing the data contained in Table 1, the following deductions have been made [1]:

1. The first two experiments demonstrate that the reaction rate does not depend on the methane partial pressure.
2. Experiments 3 and 4 show that the reaction rate decreases as the benzene increases.
3. Experiments 10 and 11 demonstrate that where there are low concentrations of toluene, the reaction rate increases with the increase in the toluene partial pressure, whilst with high concentrations of toluene, the rate remains essentially independent of the toluene partial pressure.

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Table 1
The reaction rate values obtained on a differential reactor at a temperature of 600°C

i	r_T	p_T	p_H	p_M	p_B
1	71.0	1	1	1	0
2	71.3	1	1	4	0
3	41.6	1	1	0	1
4	19.7	1	1	0	4
5	42.0	1	1	1	1
6	17.1	1	1	0	5
7	71.8	1	1	0	0
8	142.0	1	2	0	0
9	284.0	1	4	0	0
10	47.0	0.5	1	0	0
11	71.3	1	1	0	0
12	117.0	5	1	0	0
13	127.0	10	1	0	0
14	131.0	15	1	0	0
15	133.0	20	1	0	0
16	41.8	1	1	1	1

r_T is the reaction rate (g mol toluene/g-cat s)$\times 10^{10}$.
p_T is the toluene partial pressure (atm).
p_H is the hydrogen partial pressure (atm).
p_M is the methane partial pressure (atm).
p_B is the benzene partial pressure (atm).

4. Experiments 7–9 show that the reaction rate increases linearly with the hydrogen partial pressure.

By combining these observations, the following model can be proposed

$$-r_T = \frac{kK_T p_{H_2} p_T}{1 + K_B p_B + K_T p_T}. \tag{2}$$

The unknown parameters are estimated by linearizing the model

$$y = \frac{p_{H_2} p_T}{-r_T} = \frac{1}{kK_T} + \frac{K_B}{kK_T} p_B + \frac{p_T}{k} = a_0 + a_1 p_B + a_2 p_T. \tag{3}$$

This type of analysis is incorrect as will be shown in the following.

2. Alternative kinetic models building

This issue will be dealt with in greater depth elsewhere and so I will limit myself to a brief comment at this point.

The analysis employed in [1] above summarized for the model (2) selection must be avoided.

It contains two errors. The first is extremely serious: it is not possible to judge the importance of a variable and thus it is not possible to select the model form on the basis of such simplistic considerations made using a limited number of experiments changing only one variable and maintaining the other variables at a fixed level.

Take, for example, the first deduction regarding the independence of the partial pressure of methane. A methane dependency such as the following could be present in the model

$$-r_T = \frac{k p_{H_2} p_T}{1 + K_{BM} p_B p_M + \cdots}. \tag{4}$$

This dependency on methane might be small at the benzene level under consideration but it might also be greater under different conditions.

The second error is excusable but more subtle [2]. If you want to carry out statistical tests on the model, you must avoid to use for choosing the model structure the same experiments used for the statistical tests. If the contrary is the case, the degrees of freedom to be introduced into the statistical tests must be adjusted.

The possible kinetic models for heterogeneous reactions should be found by dividing the overall reaction into the elementary reaction steps and presuming that one of the intermediate steps is the slowest and therefore, controls the global reaction rate. The different alternative models are developed using the various possible reaction mechanisms and various possible paths. The best model must be chosen amongst these, using the proper experimental design.

In many practical situations, these alternative models belong to classes of families which share the same structure. For example, the following expression is obtained when the Hougen and Watson method is used to build models for toluene kinetics

$$r = \frac{k_1(p_T p_{H_2} - (p_B p_C / k_{EQ})}{(1 + \sum_{i=1} N_p k_i \prod_{j=1}^{4} p_j^{\alpha_j})^{\gamma}} \tag{5}$$

where α_j are the parameters which can assume values between 0 and 2, exponent γ can be equal to 1, 2 or 3, and N_p is the maximum number of elements which can be reasonably introduced in the model.

In such cases, it is possible to write a program [3] which automatically generates all the models with that particular structure (5). This has a twofold advantage. Firstly, it eliminates the need for a manual search for possible models and, more importantly, it gives the possibility to analyze a much larger number of alternatives congruent with the theory.

3. Selection of the experimental reactor

This point too will be dealt with in greater detail elsewhere and therefore I will again comment only briefly here.

When the calculations used to find the model parameters were performed manually and also, later, when inefficient routines and computers were employed, the experimentation was attempted with the so-called differential reactor. Using this type of reactor meant that a value for the reaction rate was obtained straightway and this was considered as a dependent variable. Furthermore, it was also hypothesized that only the dependent variable was subject to experimental error. Given these hypotheses, it thus seemed reasonable to calculate the model parameters by minimizing the sum of the squares of the discrepancies between the experimental values of the reaction rate and the model predictions.

$$S_1(\mathbf{b}) = \sum_{i=1}^{N} (r_i - r(\mathbf{x}_i, \mathbf{b}))^2 \tag{6}$$

where $\mathbf{b}$ is the vector of the model parameters and $\mathbf{x}$ the vector of the independent variables.

When it was not possible to use a differential reactor, the experiments were carried out by maintaining all of the independent variables at a fixed value with exception of the contact time for which various values were considered. The derivative was estimated by reporting the curve obtained as a function of the contact time as a plot.

Both of these alternatives should be strictly avoided. The first because it is not possible to consider the reaction rate as the only dependent variable which contains an experimental error. The second too should be avoided for the aforementioned reason. However, there are two further problems associated with it: the numerical error introduced whilst graphically calculating the derivative and the futile waste of a large number of experiments which might otherwise be put to better use in estimating the model parameters.

When an integral type reactor is being considered, then the dependent variable must be calculated by numerically integrating the reactor balance equations. Furthermore, it is not plausible that only the dependent variable be subject to experimental error. The function to be minimized therefore becomes much more complex than Eq. (6). Nevertheless, this is now possible due to the high performance levels of modern computers and the existence of programs specifically written to solve the problem of non-linear regression.

4. Basic experiments design

Careful selection of the design of the experiments is of fundamental importance to the creation of a good model. This must be carried out in three successive phases. Only the first of these will be examined here.

During this initial phase it is necessary to design and perform experiments which permit a preliminary analysis of the proposed models and the possible elimination of the least successful ones.

The traditional procedure performed the experiments by varying only one independent variable at a time whilst maintaining all of the others at a certain fixed value.

There was a double objective to this. On the one hand, it allowed a graphical representation of the experiments to be compiled or, at least, the estimation of the effects of the individual variables. On the other hand, it made the calculation of the parameters easier by linearizing the model. (See the analysis performed in the previous example as reported in [1].)

However, this choice shows the following defects:

- The number of experiments required is high compared with other alternatives and becomes prohibitive if the number of independent variables is significant.
- Possible interactions between the variables are not taken into consideration.
- The linearization of the model must be avoided if an estimation of the model parameters congruent with the statistical experimental error distribution is desired, as will be demonstrated later.

The experiment design to be used in the initial phase should be capable of covering the experimental range with the smallest possible number of experiments. Standard composite centralized designs are well suited for this.

5. Determining the model parameters

Before determining the model parameters, it is essential to discover what the statistical distribution of experimental error of the variable(s) subject to error is.

Only when this question has been answered is it possible to select the function to be minimized (or maximized).

To simplify things (and as often happens uncritically anyway), it is assumed that the only variable subject to error is the dependent variable and also that the best estimation of the parameters corresponds to the minimization of the sum of the squared discrepancies between the measured dependent variable and the model calculations.

It is important to emphasize that even with the simplistic hypothesis in which the only dependent variable is subject to error, it is not possible to manipulate the model to facilitate the calculations if the manipulation modifies the function to be optimized.

For example, it is a mistake to use the procedure adopted in [1] i.e. to linearize the model through Eq. (3) and deduce the parameters of the linearized model. Often in these cases, the error is further aggravated: once the parameters have been calculated for an assigned temperature (in this case, 600°C), the procedure is repeated for other temperatures. A regression (also linear) is then performed of the logarithm of the constants obtained at the different temperatures as a function of the inverse of the absolute temperature (since it is presumed that the kinetic constants k_s have an Arrhenius type form).

It should be obvious that this minimizes a different function from the theoretically acceptable one, and, consequentially, the value of the parameter will be different from the one which would be obtained by minimizing the appropriate function. Practical experience confirms that the numerical value of the kinetic constants obtained using this procedure can be very different from the correct one and, in fact, may often have the opposite sign.

In the most realistic scenario in which even the independent variables are subject to error, the function to be minimized will be more complex and the number of variables in the optimization will be much higher. The conceptual problem, however, remains the same.

For example, let us assume that we want to study the kinetics of toluene hydrogenation (4) using an isothermal plug flow reactor. The experimental variables for the *i*th experiment are as follows: temperature, T, contact time τ, the inlet and outlet moles of $C_6H_5CH_3$, H_2, C_6H_6, and CH_4:

$$(T,\ \tau,\ n^0_{C_6H_5CH_3},\ n^0_{H_2},\ n^0_{C_6H_6},\ n^0_{CH_4},\ n_{C_6H_5CH_3},\ n_{H_2},\ n_{C_6H_6},\ n_{CH_4})_i. \tag{7}$$

It is assumed that both the temperature and contact times can be assumed free of appreciable random errors while the other quantities have a Gaussian type error distribution with known variance.

The true unknown values of the measured values $(n^0_{C_6H_5CH_3},\ n^0_{H_2},\ n^0_{C_6H_6},\ n^0_{CH_4})_i$ are indicated as follows

$$(m^0_{C_6H_5CH_3},\ m^0_{H_2},\ m^0_{C_6H_6},\ m^0_{CH_4})_i \tag{8}$$

If these values and the values of the model parameters, **b**, were both known, then it would be possible to calculate (using a numerical integration) the value of the extent of reaction ξ_i (referred to toluene for example) at reactor outlet and, thus, the estimated values for the variables

$$(m_{C_6H_5CH_3} = m^0_{C_6H_5CH_3} - \xi_i)_i, \tag{9}$$

$$m_{H_2} = m^0_{H_2} - \xi_i)_i, \tag{10}$$

$$(m_{C_6H_6} = m^0_{C_6H_6} + \xi_i)_i, \tag{11}$$

$$(m_{CH_4} = m_{C_6H_6} + \xi_i)_i. \tag{12}$$

As in the case of ξ_i, these variables, therefore, are functions of the **b** parameters of the model and of the theoretical values (8) of the variables entering the reactor.

The **b** parameters of the model and the theoretical values (8) of the inlet variables are deduced by minimizing the function

$$S(\mathbf{b},\ m^0_{C_6H_5CH_3},\ m^0_{H_2},\ m^0_{C_6H_6},\ m^0_{CH_4}) = \sum_{j=1}^{4} \frac{(n^0_j - m^0_j)^{\mathrm{T}}(n^0_j - m^0_j)}{\sigma^2_j} + \sum_{j=1}^{4} \frac{(n_j - m_j)^{\mathrm{T}}(n_j - m_j)}{\sigma^2_j}, \tag{13}$$

where the sum is extended to the four species: $C_6H_5CH_3$, H_2, C_6H_6 and CH_4.

It is essential that the program used to find the model parameters is specifically geared towards dealing with non-linear regression problems. There is no point in using a normal optimization program because

- the methods which have to be introduced into the optimization program should take some typical characteristics of this problem into account. These include the possible correlation between the search variables for the optimum (model parameters) and the special function to be optimized (for example, the sum of the squares of the discrepancies),
- a statistical analysis of the model should be included in the program,
- the program should also contain a robust parameter estimator so that possible incorrect experiments can be detected (outliers or leverages, see after), and
- The program should be capable of providing the most suitable experiments for improving the discrimination of the models and the estimation of the parameters of the models themselves (see further).

Furthermore, it is important to modify the form with which the Arrhenius constants appear in the reaction rate. The original form is

$$k_j = k_j^0 \exp\left(-\frac{E_j}{RT}\right). \qquad (14)$$

The two parameters k and E are strongly correlated because of the imbalance in their relative influence on the model. This can create numerical difficulties for the optimization program. It is preferable therefore to substitute the previous form with the equivalent

$$k_j = \exp\left(a_j - b_j\left(\frac{1}{T} - \frac{1}{T^*}\right)\right), \qquad (15)$$

which is better balanced. In this relation, the T^* value is a mean value in the temperature range.

6. Model discrimination

Once the parameters of the various alternative models have been calculated, it is necessary to select the best one on the basis of the experiments which have been performed.

It is normally very difficult to find a single model which represents the kinetics in the experimentation range due the great flexibility arising from the structure of kinetic models for catalytic reactions. Nonetheless, it is always essential to perform some additional experiments specifically aimed at eliminating unsuitable models.

Different criteria have been suggested [4–34] which use the models themselves to predict which new experiments should be carried out in order to better discriminate between the competing models.

The most modern criteria for selecting the alternative models are based on the following three properties:

- The experiments are generated using only models which are found to be suitable on the basis of experiments performed until that time.
- The prediction made with models still competing have to be as different as possible so as to highlight wrong answers from the models.
- The prediction value alone is not a sufficient basis. The uncertainty attributed by each model to the prediction have to be also taken into account to favor those experiments where there is less uncertainty.

On a philosophical level, there are two very different approaches to generate the discrimination criterion and to decide which model to accept and which to reject. The first is a Bayesian inference which claims to be capable of assigning each model a probability of being the correct one. The second is a frequentistic approach which rejects this possibility.

From a practical point of view, the results generated are not much different if both the approaches are used with care. The most significant difference lies in the fact that the first approach can be faster but also riskier because it can lead to premature and erroneous conclusions.

7. Improvement of parameter estimation

It is also essential to devote some experiments to improve the estimation of the model parameters or of those models which have been found to be satisfactory. To do this, the models themselves are used to ascertain which experiments allow the confidence limits for the model parameters to be reduced.

There are alternative criteria in this case too [35–56]. Nevertheless, the common objective of the various methods is to reduce the volume of uncertainty for the parameters calculated using the confidence region of the parameters themselves.

8. Statistical analysis of the model

Once one or more alternative models have been generated, a statistical analysis must be performed. Its objective is as follows:

- To verify whether the model is reasonably satisfactory or whether it can be rejected.
- To check whether the parameters have been correctly estimated or whether new experiments are necessary.
- To determine if it is necessary to conduct new experiments to select a single model where several adequate alternative models exist from experiments carried out until then.
- To verify if the experimental design is adequate.
- To check if there are outliers or leverages.

It is not possible to enter into the detail of the complete statistical analysis necessary to fulfil these objectives. I will therefore limit myself to highlighting the most common errors which may be committed.

To judge if a model should be discarded or accepted an *F*-test (or a χ-test) should be performed. To do this, an estimation of the error variance has to be known and this must be compared with the MSE (mean square error, i.e. the sum of the squares of the discrepancies divided by the degrees of freedom of the model) of the model.

If the experimental F value is greater than the theoretical one deduced from the literature tables with a pre-determined risk of α, the model is discarded. If not, it is accepted.

It is a mistake to state when accepting the model that it has a probability of $1-\alpha$ of being the correct model. The only thing which can be stated is that the model is being accepted because it cannot be discarded. This is usually emphasized in statistics books.

When, on the other hand, the model is discarded, it is normally presumed that one can state that there is a pre-established risk of α of being wrong. However, this statement too is incorrect as it has recently been illustrated [57].

Whether accepting or rejecting the model, there is no quantitative control over the probability of making an error.

The calculation of the parameter confidence limits is one of the important results of the statistical analysis. Since there are normally more than two parameters in the model, it is not practical to report the curve of the confidence limits of the parameters themselves and usually an approximation is necessary.

An initial approximation comes from the calculation of the confidence limits using the model linearized by means of a Taylor expansion.

Given that these confidence limits too cannot be presented as a graph when the number of parameters is greater than two, the diameters of the ellipsoid formed by them should be calculated instead.

Normally, however, further simplification is made and instead of calculating the diameters of the ellipsoid, the latter is approximated with a rectangle. This means that the parameter confidence limits for an assigned value of risk α are represented as follows

$$l_i < b_i < u_i, \tag{16}$$

where l_i and u_i are the lower and upper limits.

Clearly it is wrong to state that the correct value for the parameters lies between these limits with a probability of $1-\alpha$. It is necessary to understand the error which would be committed by making such an assumption.

It is often maintained that this error is linked only to the approximations made to obtain the limits (16).

To understand the problem better, however, let us consider a model with two parameters. Because it is a non-linear model, the confidence limits are not ellipses. They are obtained by tracing the level lines of the function (which is the sum of the squares of the deviations) multiplied by a coefficient which depends on the α level used.

One initial error is caused by the theory that if the confidence limits for non-linear models are calculated using a value α, then they are valid in reality for a value of α' which is different from the preceding one and not known a priori.

Is it correct therefore to state that there is a probability of $1-\alpha'$ that the true value of the model parameters lies inside the level lines? No, it is not.

Many authors think that merely substituting the word *probability* with the word *confidence* is enough. In fact, it would be a conceptual error to talk about probability in this case.

It has recently been demonstrated [57] that it is also incorrect to state that one can have a confidence of $1-\alpha'$ that the correct value for the model parameters lies within the confidence limits obtained using the previous method.

If this is not possible, then of what use are the confidence limits of the parameters?

They are useful only in a negative and qualitative way: if the confidence limits are very large then it can be maintained that it is necessary to carry out a more in-depth search. When this is the case, however, the model is either unsuitable or the experimentation has not been adequate.

One analytical element which is rightly assumed to be of fundamental importance concerns the residues.

It is often said that a graphical analysis of the deviations from the experimental dependent variable and the one calculated using the model experiments highlights which have been contaminated with errors. These experiments are called *outliers* if the error refers to the value of the dependent variable and *leverages* when they refer to the portion of the independent variables.

This is true only where the dependent variable is calculated using the parameters estimated with a robust method and only if the deviations too are normalized using a robust method to estimate the variance of the error [58].

Normally, however, the deviations obtained using the parameters estimated by minimizing the sum of the squares of the deviations are used. This is not a robust method of estimation: if an experiment is contaminated by errors then the model tries to adapt itself to that experiment and so the wrong experiment is not highlighted.

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