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A new approach for sequential experimental design for model discrimination

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Abstract

Model discrimination procedures are useful tools for selection of the best mathematical models to be used to represent a specific chemical process. The present paper presents and discusses a new sequential discrimination procedure, which makes use of model probabilities and concentrates the efforts on models with higher probabilities. Model probabilities are determined based on simple statistical arguments. Four numerical examples illustrate the application of the proposed discrimination procedure. The obtained results indicate that the new procedure is able to discriminate kinetic models with fewer experiments when compared to other procedures and also indicates when model discrimination is not possible and, thus, when the sequential design must be halted. Furthermore, the speed of the proposed discrimination procedure can be controlled by tuning a design parameter which reflects the analyst's mood (confidence) towards the discrimination problem and allows for increase or decrease of the number of experiments required for model discrimination during the sequential procedure.

Keywords: Model discrimination; Experimental design; Mathematical modeling; Parameter estimation; Kinetics; Model probability

1. Introduction

Mathematical models are widely used to represent scientific theories and process behavior. Models can be applied for simulation, process design and/or improvement of the current understanding about a specific phenomenon. Frequently, several models can be developed to represent the same phenomenon. Rate equations in heterogeneous catalysis constitute a typical example (Froment, 1975). Then, very frequently the analyst has to define which model is the most suitable one for a particular application, as the final results and conclusions usually depend on the model used to perform the simulations and provide the interpretation of the analyzed problem. Sometimes, it is not possible to make a proper choice based solely on the available information, because the collected experimental data can be explained adequately by more than one model. In this case, one should perform new experiments for selection of one of the rival models. This procedure, called model discrimination, can be performed in accordance with different strategies. However, in all cases the experimental design is based on a criterion that indicates the experimental conditions where additional experiments should be performed in order to maximize the model discrimination capacity.

Frequently the model discrimination procedure is performed sequentially. Fig. 1 illustrates the steps of a typical sequential design procedure, where a single experiment is designed at each iteration. In Fig. 1, the main difference among alternative discrimination strategies is the criterion used to determine which experimental condition should be regarded as the best one and, therefore, should be used to perform the next experiment.

Hunter and Reiner (1965) proposed a very simple design criterion for sequential model discrimination. After performing N preliminary experiments, a new experimental condition $\mathbf{x}$ should be selected in order to maximize the model discrimination function, defined as

$$D(\mathbf{x}) = [\hat{y}_1(\mathbf{x}) - \hat{y}_2(\mathbf{x})]^2, \tag{1}$$

where $\hat{y}_1$ and $\hat{y}_2$ are the expected model responses for Models 1 and 2, respectively. Eq. (1) assumes that model discrimination is improved when the difference between model responses increases. For discrimination among M models, Hunter and

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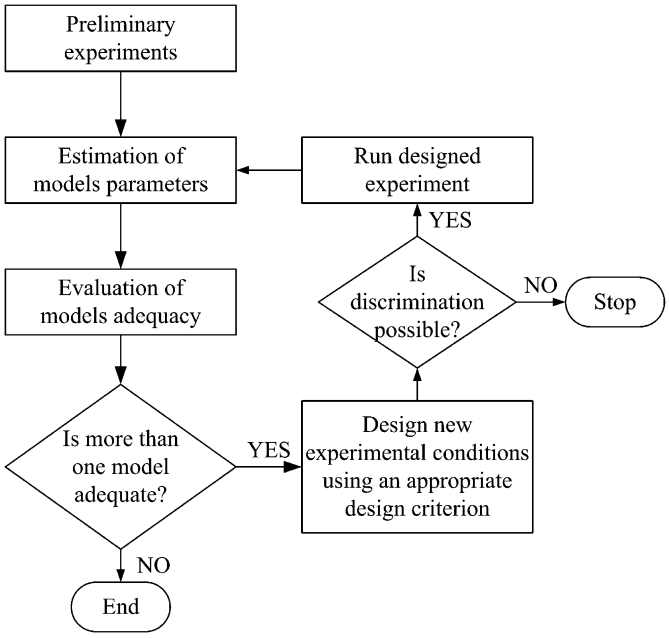

Fig. 1. Sequential experimental procedure for model discrimination.

Reiner's criterion can be extended as follows:

$$D(\mathbf{x}) = \sum_{m=1}^{M-1} \sum_{n=m+1}^{M} [\hat{y}_m(\mathbf{x}) - \hat{y}_n(\mathbf{x})]^2. \tag{2}$$

These very simple criteria do not take into account that model performances may not be the same throughout the experimental region. Model performances may be properly taken into consideration if the variances of model predictions are inserted into the design criteria, as pointed out by Box and Hill (1967). This may avoid the selection of experimental conditions where the differences among model responses are high, but model uncertainties and experimental errors are also high. In these cases, it would not be possible to distinguish model predictions even when model responses are not similar because of the large uncertainties associated with model predictions.

Based on the information theory and using a Bayesian approach, Box and Hill (1967) developed a different sequential design procedure for model discrimination. Since entropy can be used as a measure of the amount of available information about a particular system, additional experiments should be selected in order to maximize the expected change of entropy, thus maximizing the amount of information obtained about the investigated system after conduction of the additional experiments. Entropy can be defined as

$$S = -\sum_{m=1}^{M} P_{m,N} \ln P_{m,N}, \tag{3}$$

where $P_{m,N}$ is the probability that model m is the best model after N experiments. Maximization of the expected change in entropy can be attained through maximization of the following equation:

$$D(\mathbf{x}) = \sum_{m=1}^{M-1} \sum_{n=m+1}^{M} P_{m,N} P_{n,N} \times \left\{ \frac{\left[\sigma_m^2(\mathbf{x}) - \sigma_n^2(\mathbf{x})\right]^2}{\left[\sigma^2(\mathbf{x}) + \sigma_m^2(\mathbf{x})\right]\left[\sigma^2(\mathbf{x}) + \sigma_n^2(\mathbf{x})\right]} + [\hat{y}_m(\mathbf{x}) - \hat{y}_n(\mathbf{x})]^2 \left(\frac{1}{\sigma^2(\mathbf{x}) + \sigma_m^2(\mathbf{x})} + \frac{1}{\sigma^2(\mathbf{x}) + \sigma_n^2(\mathbf{x})} \right) \right\}, \tag{4}$$

where σ^2 is the experimental variance of the experimental response and σ_m^2 is the prediction variance of model response $\hat{y}_m$ at experimental condition $\mathbf{x}$. Model probabilities can be updated after conduction of the selected experiment with the aid of the Bayes' Theorem as

$$P_{m,N+1} = \frac{P_{m,N}\, p_m(\mathbf{x})}{\sum_{n=1}^{M} P_{n,N}\, p_n(\mathbf{x})}, \tag{5}$$

where $p_m(\mathbf{x})$ is the probability density function associated with the $(N+1)$th experimental observation. Assuming that model m is correct and that model deviations follow the normal distribution

$$p_m(\mathbf{x}) = \frac{1}{\sqrt{2\pi\left[\sigma^2(\mathbf{x}) + \sigma_m^2(\mathbf{x})\right]}} \times \exp\left(-\frac{\left[y_{N+1}(\mathbf{x}) - \hat{y}_{m,N+1}(\mathbf{x})\right]^2}{2\left[\sigma^2(\mathbf{x}) + \sigma_m^2(\mathbf{x})\right]} \right), \tag{6}$$

where y_{N+1} is $(N+1)$th experimental value.

The designed experimental condition should maximize Eq. (4) and the current status of the analyzed models should be updated with Eq. (5). The procedure should be repeated iteratively and halted when the probability of one of the rival models becomes higher than a certain threshold value (for instance, 0.95). A very interesting feature of this procedure is that experimental design and model evaluation are performed simultaneously (Hill, 1978), since posterior model probabilities can be used both for design and model evaluation. One problem normally associated with Bayesian approaches is that they force the selection of one of the rival models, even when all models are bad (Atkinson, 1978). For this reason, model performances should be critically evaluated at each particular iteration of the experimental design.

Dumez et al. (1977) and Atkinson (1978) commented that extensive simulation studies failed to reveal any systematic difference between experimental plans designed with either Box and Hill's or Hunter and Reiner's criteria. For this reason, Eq. (2) is usually preferred because of its simplicity.

Buzzi-Ferraris and Forzatti (1983) raised an interesting point about the performance of sequential experimental designs for model discrimination. They showed that results obtained with the Box and Hill's criterion depend on how experimental observations are ordered because of the recursive law that is used

to update model probabilities. This is unacceptable, as model probabilities should depend on the available information and not on the particular order used to present the data. They also noted that experiments can be selected in regions where differences of prediction variances are large (and not where differences of model responses are large) because of the structure of Eq. (4).

Atkinson and Fedorov (1975a) developed T-optimum designs for discrimination between two rival models when one of the two models is assumed to be the true model. This procedure was later extended for discrimination among M models (Atkinson and Fedorov, 1975b) and application of this procedure to kinetic problems can be found in Atkinson et al. (1998). The experimental conditions are then selected in order to maximize the noncentrality parameters, given as

$$\Delta_2(\mathbf{x}, \boldsymbol{\theta}_1) = \max_{\mathbf{x}} \left\{ \min_{\boldsymbol{\theta}_2} \sum_{k=1}^{N} [y_1(\mathbf{x}, \boldsymbol{\theta}_1) - y_2(\mathbf{x}, \boldsymbol{\theta}_2)]^2 \right\}, \quad (7)$$

which is the noncentrality parameter for Model 2 when Model 1 is true. As can be seen in Eq. (7), the parameters of Model 2 are estimated for every set of experimental conditions and the selected set of experimental conditions is the one that leads to the higher value of the noncentrality parameter. This may be an interesting way to initialize an experimental design, since an initial set of experiments is not required for the design. However, during sequential designs, when an initial set of experiments is available, this procedure becomes similar to the original Hunter and Reiner's procedure, as described in Eq. (1).

The assumption that one of the models is the true one is unrealistic for most practical situations, as models are always simplifications of complex phenomena and are based on certain simplifying hypotheses. To overcome this limitation, Ponce de Leon and Atkinson (1991) made use of prior probabilities and assumed that any of the rival models could be the true one, in accordance with a specified set of model probabilities, so that the new experimental condition should be selected through maximization of

$$D(\mathbf{x}) = \sum_{m=1}^{M} \sum_{\substack{n=1 \\ n \neq m}}^{M} P_m \Delta_n(\mathbf{x}, \boldsymbol{\theta}_m), \quad (8)$$

where $\Delta_n(\mathbf{x}, \boldsymbol{\theta}_m)$ is the noncentrality parameter for model n when model m is assumed to be the true one, as defined in Eq. (7), and P_m is the probability that model m is the true one. The application of this design criterion may lead to extensive computations, since the parameters of the untrue models have to be estimated for every set of experimental conditions, based on the responses of the true model with known parameters. This may constitute a serious drawback for practical use of this design criterion.

Buzzi-Ferraris and Forzatti (1983) proposed a sequential model discrimination procedure where the new experimental conditions should maximize

$$D(\mathbf{x}) = \frac{\sum_{m=1}^{M-1} \sum_{n=m+1}^{M} [\hat{y}_m(\mathbf{x}) - \hat{y}_n(\mathbf{x})]^2}{(M-1)\left[M\sigma^2(\mathbf{x}) + \sum_{m=1}^{M} \sigma_m^2(\mathbf{x})\right]}. \quad (9)$$

Eq. (9) can be obtained as the ratio between the variance of model deviations and the mean value of the model prediction variances. For discrimination between two rival models, Eq. (9) becomes

$$D_{m,n}(\mathbf{x}) = \frac{[\hat{y}_m(\mathbf{x}) - \hat{y}_n(\mathbf{x})]^2}{2\sigma^2(\mathbf{x}) + \sigma_m^2(\mathbf{x}) + \sigma_n^2(\mathbf{x})}. \quad (10)$$

Eqs. (9) and (10) can be interpreted in terms of the classical F-statistics, so that maximization of D is equivalent to maximization of the capacity to discriminate between two distinct variance terms. Different from Box and Hill's criterion, this criterion does not lead to selection of experimental conditions where differences in prediction variances are large and differences in model responses are not. Besides, the discrimination procedure defined by Eqs. (9) and (10) is not affected by the order of the experimental observations, as it should be expected. However, it is necessary to rely on additional statistical tests to evaluate the model adequacy after each discrimination step, which is not necessary when the original Box and Hill's procedure is used, as model probabilities are updated automatically during the experimental design.

It is possible to eliminate the worst models faster if the experimental conditions are designed to maximize Eq. (10), instead of Eq. (9). In Eq. (9), as also happens in Eqs. (2) and (4), a new set of experimental conditions can be selected in regions where the divergence among all rival models is not very large. In practice, it may be preferable to select the experimental conditions in experimental regions where at least one of the models can be discriminated from the rest and, therefore, eliminated from the set of plausible models.

Eqs. (9) and (10) were extended to allow for analysis of models that contain multiple responses (Buzzi-Ferraris et al., 1984). The design criterion consists in finding the experimental conditions that maximize

$$D_{m,n}(\mathbf{x}) = [\hat{\mathbf{y}}_m(\mathbf{x}) - \hat{\mathbf{y}}_n(\mathbf{x})]^{\mathrm{T}} \mathbf{V}_{m,n}^{-1}(\mathbf{x}) [\hat{\mathbf{y}}_m(\mathbf{x}) - \hat{\mathbf{y}}_n(\mathbf{x})], \quad (11)$$

where m and n stand for the reference models, $\hat{\mathbf{y}}_m$ is a vector of response variables for model m and $\mathbf{V}_{m,n}$ is defined as

$$\mathbf{V}_{m,n}(\mathbf{x}) = 2\mathbf{V}(\mathbf{x}) + \mathbf{V}_m(\mathbf{x}) + \mathbf{V}_n(\mathbf{x}), \quad (12)$$

where $\mathbf{V}$ is the matrix of experimental variances of the measured response variables and $\mathbf{V}_m$ is the matrix of prediction variances of responses calculated from model m.

Buzzi-Ferraris et al. (1990) presented an improved version of Eq. (11) for discriminating among rival multiple response models. The new set of experimental conditions should be selected in order to maximize the expected value of the divergence, given by

$$D_{m,n}(\mathbf{x}) = [\hat{\mathbf{y}}_m(\mathbf{x}) - \hat{\mathbf{y}}_n(\mathbf{x})]^{\mathrm{T}} \mathbf{V}_{m,n}^{-1}(\mathbf{x}) [\hat{\mathbf{y}}_m(\mathbf{x}) - \hat{\mathbf{y}}_n(\mathbf{x})] + \mathrm{tr}\left(2\mathbf{V}(\mathbf{x})\mathbf{V}_{m,n}^{-1}(\mathbf{x})\right). \quad (13)$$

In order to evaluate whether it would be possible to discriminate among the rival models, Buzzi-Ferraris and Forzatti (1983) and Buzzi-Ferraris et al. (1984, 1990) suggested that the optimum discriminant value obtained from Eqs. (9), (11) or (13)

should always be smaller than the number of model responses; otherwise, the procedure should be halted. This is because the discriminant values are expected to follow the χ^2-distribution when the model performances are similar.

Although the criteria developed by Buzzi-Ferraris and Forzatti (1983) and Buzzi-Ferraris et al. (1984, 1990) do overcome the difficulties observed during actual implementation of the original Box and Hill's procedure, the fact is that the use of model probabilities is appealing for a number of reasons. First, model analysis and comparison of model responses become much simpler and unambiguous when a quantitative measure of model adequacy can be assigned to the analyze models. Second, it sounds reasonable to say that efforts should be concentrated on the discrimination of the most probable models, and not on discrimination of the least probable ones. Therefore, the divergence criterion should be somehow weighted by model probabilities.

For this reason, a new procedure for model discrimination is sought here, based on the definition of model probabilities. However, model probabilities should not depend on how the experimental observations are ordered. Therefore, the use of iterative procedures should be avoided for assignment of model probabilities.

Another interesting point regards the interaction between the analyst and the discrimination problem. According to the previously published criteria, the sequence of designed experiments depends solely on the experimental responses, so that the designed experiments do not reflect the analyst's confidence towards the discrimination problem. For instance, experimental designs for discrimination among empirical rival models should be small and should not require too much effort. However, when rival models are based on distinct mechanistic theories and model performances are used to select the "true" mechanism, one may be very cautions about discarding a model from the discrimination procedure. This shows that the analyst may be liable to accept different levels of "risk" during the discrimination procedure and that the design criterion should reflect the analyst's mood towards the discrimination problem.

The main purpose of this work is to introduce a new procedure for model discrimination, which makes use of the χ^2-distribution to estimate probabilities for each model. The probabilities are calculated using the Tsallis' concept of entropy (Tsallis, 1988), where a certain parameter (Z) controls the degree of risk that the analyst is ready to accept during the discrimination procedure. The procedure reported here is an improved version of the one developed by Oliveira (1997) and used by Dariva et al. (1998) for discrimination among thermodynamic models.

2. Methodology

2.1. Model probabilities

Let us assume that model m is indeed a perfect model, e.g. prediction errors can be explained in terms of the experimental inaccuracies and that residuals follow a standard normal distribution and are not correlated. In this way, the weighted sum of the squares of the residuals for the model m, defined by

$$\mathrm{SS}_m \equiv \sum_{j=1}^{N}\sum_{i=1}^{NY}\left(\frac{y_{i,j}(\mathbf{x})-\hat{y}_{i,j,m}(\mathbf{x})}{\sigma_{i,j}(\mathbf{x})}\right)^2 \tag{14}$$

approximately follows a χ^2-distribution with $\upsilon = \mathrm{NE} - \mathrm{NP}_m$ degrees of freedom, where NE is the number of experimental points and NP_m is the number of parameters of model m. Of course, this is an approximation because, even when model m is perfect, experimental data may be corrupted by errors that do not necessarily follow the normal distribution. Similarly, model parameters and predictions are also corrupted to some extent. Besides, the assumption of independence is questionable, although the validity of these hypotheses can be rarely checked without intensive replication work. If data are not independent, Eq. (14) can be extended in a straightforward manner to include correlations, which is not pursued here for the sake of simplicity.

The very basic idea behind the use of the χ^2-distribution is that "bad" models are likely to exhibit large values of SS_m. In other words, if the model behaves well, one should not expect to obtain high values of SS_m. Then, a value can be assigned to each model as

$$\phi_m \equiv 1 - p\left[\chi^2_\upsilon \leqslant \mathrm{SS}_m\right], \tag{15}$$

where χ^2 represents the chi-square distribution with υ degrees of freedom. Eq. (15) quantifies the adequacy of model m to represent the available experimental data. In other words, the better the model adequacy, the lower the value of SS_m. Relative probabilities are calculated from ϕ_m for each model as

$$P_m \equiv \frac{\phi_m}{\sum_{n=1}^{M}\phi_m}. \tag{16}$$

P_m can be regarded as quantitative measures of model adequacy and as weights during the experimental design. One should observe that model probabilities are not sensitive to the order of experimental data. Therefore, an unambiguous set of model probabilities can be obtained for each set of experimental data, regardless of the history of the sequential experimental design.

2.2. Design criterion

The discriminating function to be maximized can be defined as

$$D_{m,n}(\mathbf{x}) = (P_m P_n)^z \frac{[\hat{y}_m(\mathbf{x}) - \hat{y}_n(\mathbf{x})]^2}{2\sigma^2(\mathbf{x}) + \sigma_m^2(\mathbf{x}) + \sigma_n^2(\mathbf{x})}, \tag{17}$$

where m and n vary from 1 to M, where M is the number of rival models. Experimental conditions that lead to the highest value of $D_{m,n}$, for any pair of models, are selected for the next experiment. This way, bad models can be eliminated soon during the sequential design which may be seen as an important feature of the proposed procedure. This criterion comprises two contributions: a product of model probabilities, determined solely

from past experience, and a variance-weighted divergence term, which also depends on previous data (through model parameters) and selected experimental conditions for the next experiment. Note that, in general, experimental and predictions variances may be a function of the experimental settings. One should also observe that $D_{m,n}$ follows a classical χ^2-statistics under assumptions of normal fluctuations. Again, Eq. (17) can be extended in a straightforward manner for multiple response models when model responses are correlated:

$$D_{m,n}(\mathbf{x}) = (P_m P_n)^z [\hat{\mathbf{y}}_m(\mathbf{x}) - \hat{\mathbf{y}}_n(\mathbf{x})]^{\mathrm{T}} \mathbf{V}_{m,n}^{-1} \times [\hat{\mathbf{y}}_m(\mathbf{x}) - \hat{\mathbf{y}}_n(\mathbf{x})], \tag{18}$$

where $\mathbf{V}_{m,n}$ is defined by Eq. (12).

Eqs. (17) and (18) are similar to Eqs. (10) and (11), respectively, but the inclusion of the probability factors tends to concentrate the experimental efforts on the discrimination of the most probable models.

The parameter Z introduced in Eq. (17) resembles Tsallis' parameter used for generalization of the entropy and information content (Tsallis, 1988). Values of $Z > 1$ accentuate model differences and therefore may be used to bias the sequential procedure towards discrimination of the best models. Values of $Z < 1$ tend to equalize the model probabilities and to neglect the model performance during the experimental design. In a certain sense, Z can be used to fit the risk that the user is liable to accept during the model selection. High values of Z tend to increase the bet on the selection of the best models, leading to model selection with fewer experiments. Therefore, large Z-values correspond to acceptance of higher risks. Low values of Z tend to decrease the bet on selection of the best models, usually leading to large experimental data sets. Therefore, low Z-values correspond to a conservative mood towards the discrimination problem.

2.3. Termination criteria

Some of the models are expected to be discarded along the discrimination procedure. This should occur when, after the execution of the additional experiment and re-estimation of model parameters, the relative model probability falls below a predefined value (typically in the range of 1–5%). Initial relative probabilities can be calculated using an initial set of available experiments. The maximum of $D_{m,n}(\mathbf{x})$ can be searched with the help of suitable optimization routines, although acceptable designs can be achieved by direct search on a discretized experimental grid.

The experimental design procedure terminates when, after execution of the k-th experiment, one of the models reaches a relative probability that is higher than a predefined value (e.g. 95%). This is a desirable scenario, since one of the models is selected as the best among all proposed models. The discrimination procedure should also be halted when further discrimination between two or more models is not possible. This can be checked by calculating the ratio between model divergence and prediction variances, as

$$R_{m,n}(\mathbf{x}) = \frac{[\hat{y}_m(\mathbf{x}) - \hat{y}_n(\mathbf{x})]^2}{2\sigma^2(\mathbf{x}) + \sigma_m^2(\mathbf{x}) + \sigma_n^2(x)} \tag{19}$$

for single response models. For multiresponse models this ratio is defined as

$$R_{m,n}(\mathbf{x}) = [\hat{\mathbf{y}}_m(\mathbf{x}) - \hat{\mathbf{y}}_n(\mathbf{x})]^{\mathrm{T}} \mathbf{V}_{m,n}^{-1} [\hat{\mathbf{y}}_m(\mathbf{x}) - \hat{\mathbf{y}}_n(\mathbf{x})]. \tag{20}$$

As done by Buzzi-Ferraris and Forzatti (1983) and Buzzi-Ferraris et al. (1984, 1990), when the value of $R_{m,n}$ in Eqs. (19) and (20) is smaller than the number of model responses, the discrimination procedure should be halted, since it becomes impossible to discriminate between the remaining models on solid statistical arguments.

3. Numerical examples and discussion

In the following examples, one of the models is always assumed to be the true model, and data are generated from it. Model responses are perturbed with a normally distributed experimental error computed with the help of the software Statistica (1995). When one model reaches a relative probability higher than 97.5%, the discrimination procedure is successfully finished with one model selected as the best one. Besides, if one model assumes a relative probability less than 2.5% during model discrimination procedure, this model is discarded from the experimental design.

3.1. Example 1: methanol synthesis

This example has been reported by Buzzi-Ferraris and Forzatti (1983), and regards the conversion of synthesis gas to methanol in a differential reactor. The discrimination procedure is performed to select the best model among five alternative kinetic models, which were derived assuming different kinetic mechanisms. The five derived models derived are listed below:

Model 1:

$$y_1 = \frac{x_1 x_2^2 - x_3/K_{\mathrm{eq}}}{(K_{1,1} + K_{2,1}x_1 + K_{3,1}x_2 + K_{4,1}x_3)^2}, \tag{21.a}$$

Model 2:

$$y_2 = \frac{x_1 x_2^2 - x_3 K_{\mathrm{eq}}}{(K_{1,2} + K_{2,2}x_1 + K_{3,2}x_2 + K_{4,2}x_1x_2)}, \tag{21.b}$$

Model 3:

$$y_3 = \frac{x_1 x_2^2 - x_3/K_{\mathrm{eq}}}{(K_{1,3} + K_{2,3}x_3 + K_{3,3}x_2 + K_{4,3}x_3/x_2)x_2^2}, \tag{21.c}$$

Model 4:

$$y_4 = \frac{x_1 x_2^2 - x_3/K_{\mathrm{eq}}}{x_2(K_{1,4} + K_{2,4}x_1 + K_{3,4}x_3/x_2 + K_{4,4}x_3)^2}, \tag{21.d}$$

Model 5:

$$y_5 = \frac{x_1 x_2^2 - x_3/K_{\mathrm{eq}}}{(K_{1,5} + K_{2,5}x_2 + K_{3,5}x_1x_2 + K_{4,5}x_3)^2}, \tag{21.e}$$

Table 1
Eight preliminary experiments in Example 1

Run	x_1	x_2	x_3	y (10^2)
1	17	210	6.0	1.051
2	23	210	6.0	1.553
3	17	240	6.0	1.982
4	23	240	6.0	2.355
5	17	210	9.0	0.132
6	23	210	9.0	0.791
7	17	240	9.0	0.843
8	23	240	9.0	1.235

where y_i is the reaction rate from model i, x_1, x_2 and x_3 are the pressures of carbon monoxide, hydrogen and methanol, respectively.

Model 5 is assumed to be the correct model. Experimental data were corrupted with a normal deviation with zero mean and variance 4×10^{-6}. Actual parameters used to generate the experimental data were $K_{1,5}=1704$, $K_{2,5}=4.25$, $K_{3,5}=0.241$, $K_{4,5}=444.6$, $K_{eq}=1.7\times10^{-5}$, inside the experimental region: $15\leqslant x_1\leqslant 25$, $200\leqslant x_2\leqslant 250$, $5\leqslant x_3\leqslant 10$. Eight preliminary experiments are used for initial parameter estimation. Experimental design is performed over the three-dimensional grid defined for variables x_1, x_2 and x_3 which were divided, respectively, in 10, 50 and 50 subintervals. The initial experiments were defined in accordance with a full 2^3 factorial design, as usually performed in similar tests, as shown in Table 1. Sequentially designed experiments are presented in Tables 2 and 3 for Z equal to 0 and 1, respectively.

After execution of the preliminary experiments, the posterior probability of Models 2 and 3 are very low, which means that Models 2 and 3 will probably be discarded after execution of additional experiments. When Z is set to zero, the model probabilities are not taken into account during experimental design and an experiment is selected for discrimination between Models 2 and 3, which are the least probable models. This indicates that the use of model probabilities can be very helpful for experimental design. After the execution of the first designed experiment, Model 2 is discarded from the experimental design, since its probability becomes smaller than 2.5%. The two sequentially designed experiments were then selected for discrimination between Models 3 and 5. The probability of Model 3 oscillates and after three sequentially designed experiments, the procedure is halted because R value becomes smaller than 1.

When Z is set to 1, all designed experiments are selected for discrimination between Models 3 and 5. Again, after one designed experiment, Model 2 is discarded from the discrimination procedure, although no specific experiments are designed for discrimination of Model 2. Again, after three designed experiments, the procedure is halted because R becomes smaller than 1.

This is an example where model discrimination is not achievable. The procedure promptly indicates that discrimination procedure should be stopped. Consequently, the problem should be reviewed and/or the experimental region should be modified. In addition, parameter estimates do not show any statistical significance, as it can be seen in Table 4. Experiments for precise parameter estimation should also be performed in this case.

This problem was first analyzed by Buzzi-Ferraris and Forzatti (1983). Based on the design criterion defined in Eq. (9), they showed that it was necessary to design three experiments to conclude that the discrimination among these models was not achievable, with the exception of Model 2, which could be discarded. For the sake of comparison, using the eight preliminary experiments from Buzzi-Ferraris and Forzatti (1983), the procedure developed here leads to presented results in Tables 5 and 6, for Z values of 0 and 1, respectively.

When Z was set to 0, three additional experiments were designed: two of them were selected for discrimination between Models 2 and 3, the worse models. But when Z was set to 1, just two designed experiments were necessary, both for discrimination between Models 3 and 4. However, when Z was set to 1, Model 2 could not be discarded after execution of the two designed experiments. Anyway, probabilities of Models 2 and 3 were much smaller than the probabilities of the others models, indicating that these two models are likely to be the worse ones.

This example shows that the procedure developed here is able to select the best experiment in the grid of available experiments for model discrimination and can promptly halt the discrimination procedure when the discrimination among models is not possible. When the termination criterion R leads to interruption of the sequential design, the experimenter can review the experimental setup and the design region in order to improve the precision of model predictions and enhance model differences.

3.2. Example 2: multiresponse models

Discrimination is now performed with four chemical kinetic models, each having two responses, as proposed by Buzzi-Ferraris et al. (1984):

Model 1:

$$y_1=\frac{K_{1,1}x_1x_2}{1+K_{3,1}x_1+K_{4,1}x_2},\quad y_2=\frac{K_{2,1}x_1x_2}{1+K_{3,1}x_1+K_{4,1}x_2}, \tag{22.a}$$

Model 2:

$$y_1=\frac{K_{1,2}x_1x_2}{(1+K_{3,2}x_1+K_{4,2}x_2)^2},\quad y_2=\frac{K_{2,2}x_1x_2}{(1+K_{3,2}x_1)^2}, \tag{22.b}$$

Model 3:

$$y_1=\frac{K_{1,3}x_1x_2}{(1+K_{3,3}x_2)^2},\quad y_2=\frac{K_{2,3}x_1x_2}{(1+K_{4,3}x_1)^2}, \tag{22.c}$$

Model 4:

$$y_1=\frac{K_{1,4}x_1x_2}{1+K_{3,4}x_1+K_{4,4}x_2},\quad y_2=\frac{K_{2,4}x_1x_2}{1+K_{3,4}x_1}. \tag{22.d}$$

In this case data is generated from Model 1 with parameters $K_{1,1}=0.1$, $K_{2,1}=0.01$, $K_{3,1}=0.1$ and $K_{4,1}=0.01$. Experimental variances are set to 0.35 for y_1 and 2.3×10^{-3} for y_2. The errors of experimental responses are assumed to be independent from

Table 2
Sequentially designed experiments in Example 1 with $Z = 0$

Run	x_1	x_2	x_3	y (10^2)	R (m, n)	P_1	P_2	P_3	P_4	P_5
1–8	–	–	–	–	–	27.3	10.2	6.9	27.3	28.2
9	15	212	10.0	0.374	4.5 (2,3)	26.6	0.2	17.9	27.5	27.8
10	25	236	5.2	2.872	1.1 (3,5)	29.5	0.0	9.7	30.2	30.5
11	15	243	5.2	1.655	1.2 (3,5)	26.4	0.1	19.3	27.8	26.4
12	15	250	5.0	–	0.3 (3,5)	–	–	–	–	–

Table 3
Sequentially designed experiments in Example 1 with $Z = 1$

Run	x_1	x_2	x_3	y (10^2)	R (m, n)	P_1	P_2	P_3	P_4	P_5
1–8	–	–	–	–	–	27.3	10.2	6.9	27.3	28.2
9	15	200	10.0	0.051	3.1 (3,5)	28.7	0.6	11.4	29.4	29.9
10	25	237	5.3	2.786	1.3 (3,5)	30.6	0.3	6.5	31.2	31.4
11	15	243	5.0	1.792	2.6 (3,5)	28.7	0.6	12.5	29.6	28.6
12	25	237	5.0	–	0.4 (3,5)	–	–	–	–	–

Table 4
Parameter estimates and standard deviation for all five models in Example 1

	Model 1	Model 2	Model 3	Model 4	Model 5
K_1	3736	249268000	−3997	180.73	4610
σ_1	2954	449355000	8704	47.68	2740
K_2	41.01	−8866530	−865	2.62	−7.72
σ_2	25.81	20610100	1303	1.68	10.51
K_3	−4.10	−953378	16.54	10910	0.17
σ_3	11.16	1868370	35.96	6433	0.11
K_4	466.8	40137	240959	−15.53	467.2
σ_4	136.18	85959	318644	26.83	136.7
K_5	1.79	1.45	2.47	1.83	1.80
σ_5	0.28	0.15	1.11	0.32	0.28

Table 5
Sequentially designed experiments starting with data from Buzzi-Ferraris and Forzatti (1983) and with $Z = 0$

Run	x_1	x_2	x_3	y (10^2)	R (m, n)	P_1	P_2	P_3	P_4	P_5
1–8	–	–	–	–	–	24.2	17.3	2.8	30.9	24.8
9	15	209	10.0	0.039	3.7 (2,3)	29.3	3.4	5.6	31.4	30.3
10	25	237	5.2	2.762	2.5 (2,3)	30.2	0.4	7.7	31.4	30.3
11	15	232	5.0	1.518	1.5 (3,4)	29.2	0.7	10.6	30.3	29.2
12	15	236	5.3		0.4 (3,5)	–	–	–	–	–

Table 6
Sequentially designed experiments starting with data from Buzzi-Ferraris and Forzatti (1983) and with $Z = 1$

Run	x_1	x_2	x_3	y (10^2)	R (m, n)	P_1	P_2	P_3	P_4	P_5
1–8	–	–	–	–	–	24.2	17.3	2.8	30.9	24.8
9	15	206	10.0	0.001	2.2 (3,4)	29.4	3.0	5.6	31.5	30.5
10	15	228	5.5	1.090	1.0 (3,4)	26.0	5.7	13.7	27.9	26.8
11	25	241	5.2	–	0.8 (3,4)	–	–	–	–	–

each other. Five initial experiments are performed in accordance with a standard 2^2 full factorial design, as shown in Table 7. The sequentially designed experiments (Tables 8 and 9) are selected from an extended experimental grid where $5.0 \leqslant x_1 \leqslant 55.0$ and $5.0 \leqslant x_2 \leqslant 55.0$ and divided in 250 intervals for each variable.

After the execution of the five initially designed experiments, Models 1 and 4 present similar probabilities. When parameter Z is set to 0, the first designed experiment is selected to perform discrimination between Models 2 and 4. With six experiments, Model 4 assumes the higher probability and Model 2 assumes the lower probability among all models. The next designed experiment is selected again for discrimination between Models 2 and 4 and the execution of this experiment leads to rejection of Model 4. The discrimination power between Models 2 and 4 as a function of the experimental conditions after execution of five preliminary experiments is shown in Fig. 2. After execution of the first additional experiment the discrimination power is changed, as shown in Fig. 3.

Fig. 4 shows the discrimination power as a function of the experimental conditions after execution of two designed experiments. In this case, the next designed experiment is selected to perform discrimination between Models 1 and 2. After execution of this experiment, Model 1 reaches a probability that is very close to 100% and the discrimination procedure is terminated.

When parameter Z is set to 1 (Table 9) the first designed experiment is selected to perform discrimination between Models 1 and 4, which are the models with highest probabilities among all models. After execution of this experiment Model 1 reaches a probability that is very close to 100%, and the discrimination procedure terminates. Fig. 5 shows the discrimination power as a function of experimental conditions for discrimination of Models 1 and 4. It can be seen that the values of D when the parameter Z is equal 1 are lower because the variance weighted term is multiplied by the model probabilities, which does not happen when the parameter Z is equal to 0.

With the proposed procedure it is possible to discriminate among the rival models with three additional experiments, when Z is set to 0. The procedure is accelerated when Z is set to 1 and the discrimination is obtained with only one additional experiment. The use of higher values of parameter Z leads to discrimination of Models 1 and 4, as in the previously analyzed example. This example was first reported by Buzzi-Ferraris et al. (1984) using the criteria defined in Eq. (11), with nine initial experiments and more 10 designed experiments.

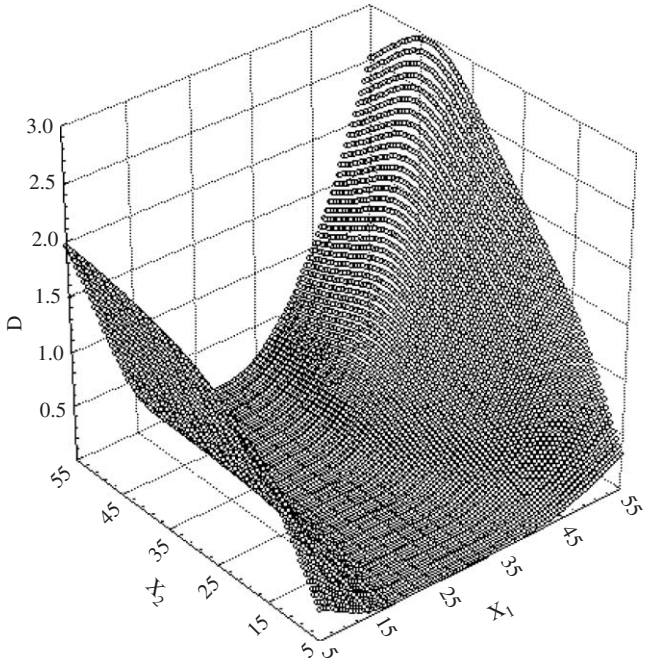

Fig. 2. Discrimination power between Models 2 and 4 after execution of the preliminary experiments in Example 2 with Z equal to 0.

Table 7
Sequence of preliminary experiments for Example 2

Run	x_1	x_2	y_1	y_2
1	20.0	20.0	13.443	1.299
2	30.0	20.0	13.817	1.433
3	20.0	30.0	17.809	1.885
4	30.0	30.0	21.139	2.118
5	25.0	25.0	16.039	1.635

Table 8
Sequence of designed experiments with $Z = 0$

Run	x_1	x_2	y_1	y_2	R (m, n)	P_1	P_2	P_3	P_4
1–5	–	–	–	–	–	30.4	23.7	16.4	29.5
6	55.0	43.2	34.507	3.420	2.96 (2,4)	37.0	8.2	11.0	43.9
7	5.0	55.0	13.954	1.309	14.4 (2,4)	61.3	24.8	13.8	0.1
8	28.4	55.0	35.485	3.553	21.7 (1,2)	100.0	0.0	0.0	0.0

Table 9
Sequence of designed experiments with $Z = 1$

Run	x_1	x_2	y_1	y_2	R (m, n)	P_1	P_2	P_3	P_4
1–5	–	–	–	–	–	30.4	23.7	16.4	29.5
6	18.0	55.0	28.989	2.902	2.84 (1,4)	100.0	0.0	0.0	0.0

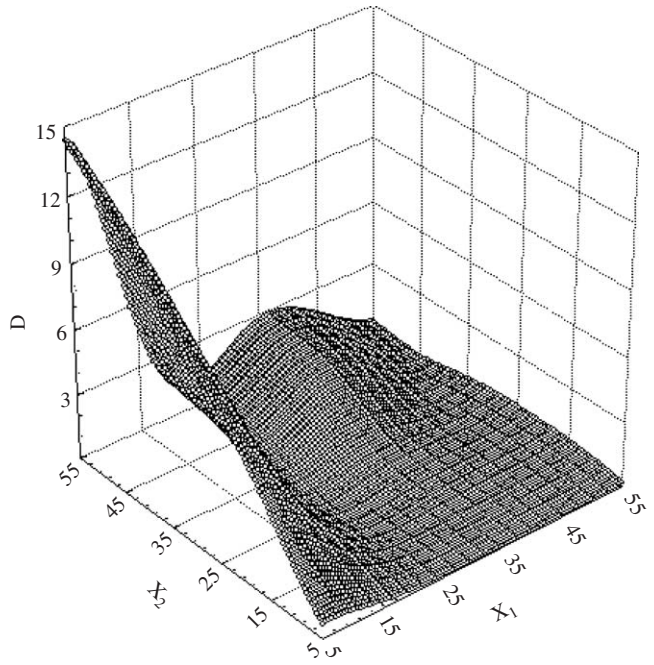

Fig. 3. Discrimination power between Models 2 and 4 after execution of the first designed experiment in Example 2 with Z equal to 0.

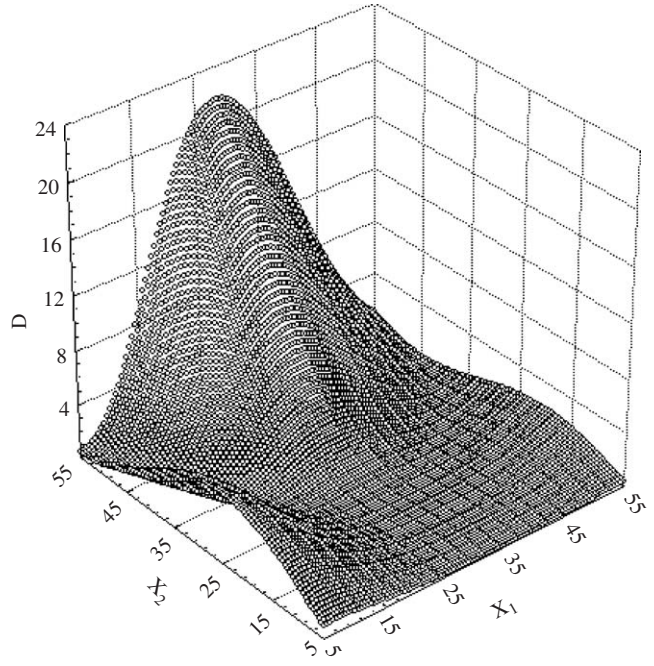

Fig. 4. Discrimination power between Models 1 and 2 after execution of the second designed experiment in Example 2 with Z equal to 0.

3.3. Example 3: water–gas shift reaction

The water–gas shift reaction (WGSR) constitutes a very important industrial process and finds applications in many fields, such as synthesis of ammonia (Levent, 2001), the development of fuel cell (Choi and Stenger, 2003; Koryabkina et al., 2003) and production of hydrogen (Amadeo and Laborde, 1995). This

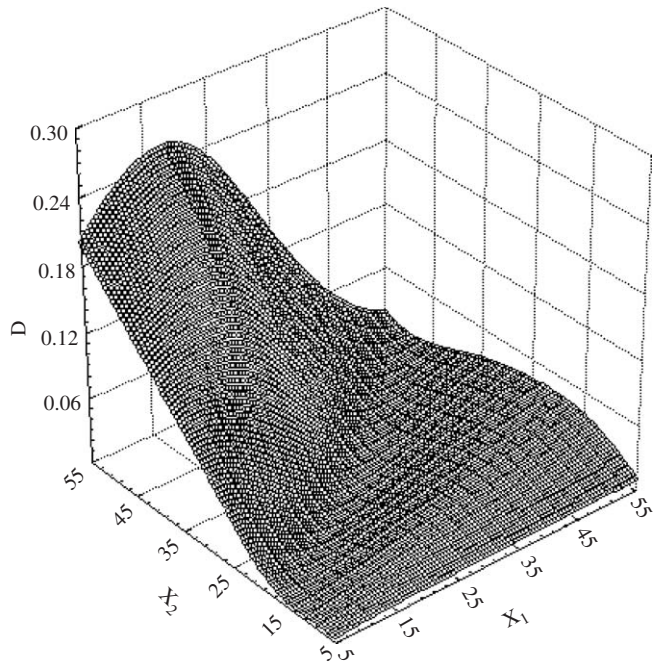

Fig. 5. Discrimination power between Models 1 and 4 after execution of the preliminary experiments in Example 2 with Z equal to 1.

reaction combines carbon monoxide and water to produce carbon dioxide and hydrogen according to the stoichometric equation

$$CO + H_2O \leftrightarrows CO_2 + H_2.$$

Due to the wide range of operations conditions (temperature, pressure and reagent concentration) in which the WGSR occurs, a large number of models can be found for description of the reaction rate. Some of the models reported in literature (Amadeo and Laborde, 1995; Levent, 2001; Choi and Stenger, 2003; Koryabkina et al., 2003) are listed below:

Model 1:

$$r = \frac{k p_{CO} p_{H_2O}(1-\beta)}{(1 + K_{CO} p_{CO} + K_{H_2O} p_{H_2O} + K_{CO_2} p_{CO_2} + K_{H_2} p_{H_2})^2}, \tag{23.a}$$

Model 2:

$$r = \frac{k p_{CO} p_{H_2O}(1-\beta)}{1 + K_{CO} p_{CO} + K_{H_2O} p_{H_2O} + K_{CO_2} p_{CO_2} + K_{H_2} p_{H_2}}, \tag{23.b}$$

Model 3:

$$r = \frac{k p_{CO} \sqrt{p_{H_2O}}(1-\beta)}{1 + K_{CO} p_{CO} + K_{H_2O} p_{H_2O} + K_{CO_2} p_{CO_2} + K_{H_2} p_{H_2}}, \tag{23.c}$$

Model 4:

$$r = \frac{k p_{CO} p_{H_2O}(1-\beta)}{1 + K_{H_2O} p_{H_2O} + K_{CO_2} p_{CO_2}}, \tag{23.d}$$

Table 10
Preliminary experiments in Example 3

Run	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r (10^3)
1	0.25	0.25	0.25	0.25	3.6908
2	0.25	0.25	0.50	0.50	1.8486
3	0.25	0.50	0.25	0.50	4.9220
4	0.25	0.50	0.50	0.25	4.3712
5	0.50	0.25	0.25	0.50	2.9268
6	0.50	0.25	0.50	0.25	4.3868
7	0.50	0.50	0.25	0.25	6.3938
8	0.50	0.50	0.50	0.50	4.2412

Model 5:

$$r = \frac{k p_{CO}(1-\beta)}{1 + K_{H_2CO_2} p_{H_2} p_{CO_2}/p_{H_2O} + K_{H_2} p_{H_2} + K_{H_2O} p_{H_2O} + K_{CO_2} p_{CO_2}}, \tag{23.e}$$

Model 6:

$$r = \frac{k p_{H_2O}(1-\beta)}{1 + K p_{H_2O}/p_{H_2}}, \tag{23.f}$$

Model 7:

$$r = \frac{k_1 k_2 p_{CO} p_{H_2O}(1-\beta)}{k_1 p_{CO} + k_2 p_{H_2O} + k_3 p_{CO_2}}, \tag{23.g}$$

Model 8:

$$r = \frac{k_1 k_2 p_{CO} p_{H_2O}(1-\beta)}{k_1 p_{CO} + k_2 p_{H_2O} + k_3 p_{CO_2} + k_4 p_{H_2}}, \tag{23.h}$$

Model 9:

$$r = \frac{k p_{CO} p_{H_2O}(1-\beta)}{K p_{H_2O} + p_{CO}}, \tag{23.i}$$

Model 10:

$$r = \frac{k p_{H_2O}(1-\beta)}{K p_{H_2O} + p_{CO}}, \tag{23.j}$$

Model 11:

$$r = k_1 p_{CO}^m p_{H_2O}^n p_{CO_2}^p p_{H_2}^q (1-\beta), \tag{23.k}$$

Model 12:

$$r = k_1 p_{CO}^m p_{H_2O}^n (1-\beta), \tag{23.l}$$

Model 13:

$$r = k_1 p_{CO} p_{H_2O}(1-\beta), \tag{23.m}$$

where β measures the proximity of the equilibrium, defined as

$$\beta = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O} K_{eq}} \tag{24}$$

and the equilibrium constant K_{eq} is calculated with a simplified equation (Choi and Stenger, 2003):

$$K_{eq} = \exp(4577.8/T - 4.33). \tag{25}$$

Models 1–6 are Langmuir type rate expressions, Models 7–10 are derived from redox mechanisms, Models 11 and 12 are power-law type equations and Model 13 is an elementary rate expression.

For the purpose of model discrimination, Model 1 is assumed here as the true model. The model parameters are presented by Amadeo and Laborde (1995) as functions of temperature. In this example, temperature is fixed at 200 °C and the parameter values are $k = 0.352\,\text{mol g}^{-1}\,\text{s}^{-1}\,\text{atm}^{-2}$, $K_{CO} = 2.726\,\text{atm}^{-1}$, $K_{H_2O} = 0.559\,\text{atm}^{-1}$, $K_{CO_2} = 0.532\,\text{atm}^{-1}$ and $K_{H_2} = 1.459\,\text{atm}^{-1}$. The calculated rate is given in $\text{mol g}^{-1}\,\text{s}^{-1}$ and all partial pressures are given in atm. Experiments are simulated from Model 1 and output variables are corrupted with a normal deviation with zero mean and variance of 1×10^{-6}. Preliminary experiments are shown in Table 10 and follow a standard 2^3 full factorial design.

The sequentially designed experiments are selected from a discrete experimental grid, where each variable (p_{CO}, p_{H_2O}, p_{CO_2} and p_{H_2}) is allowed to vary from 0.05 to 1.00, in steps of 0.05. Eq. (18) is evaluated at every point within the discrete experimental grid and for every pair of models. The new selected experimental condition is the one where Eq. (18) achieves its highest value for a particular pair of models.

Table 11 shows the sequentially designed experiments when Z is set to 0. In this case, the relative probabilities of models are not considered in the design of the experiments and are only used for model evaluation, as shown in Table 12 . The underline indicates that the analyzed model was removed from the design because of the low probabilities.

Models 4, 10 and 13 were discarded after the execution of the preliminary experiments. Model 6 was discarded after execution of the first designed experiment. Model 5 was discarded, after three designed experiments. Model 9 was discarded after execution of the fourth designed experiment, which was selected for discrimination between Models 1 and 9. Models 7 and 12 were discarded only after execution of seven designed experiments. Model 11 was discarded after one additional experiment and, subsequently, Model 3, which had the highest relative probability, was discarded after execution of the experiment selected for discrimination between Models 1 and 3. After execution of two additional experiments, both selected for discrimination between Models 1 and 8, the discrimination procedure is terminated with the indication of Model 1 as the best one.

Table 11
Sequentially designed experiments in Example 3 with $Z = 0$

Run	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r ($\times 10^3$)	R (m, n)
9	0.05	1.00	0.05	0.65	1.323	32.5 (5,6)
10	0.55	0.65	0.05	1.00	6.699	21.2 (5,9)
11	1.00	0.45	0.35	0.30	6.668	10.6 (1,5)
12	1.00	1.00	1.00	1.00	7.254	6.9 (1,9)
13	0.10	0.20	0.05	0.05	2.739	7.2 (2,11)
14	0.95	1.00	0.30	0.55	10.901	5.0 (8,12)
15	0.60	0.80	0.05	0.05	17.130	7.5 (1,12)
16	1.00	0.35	0.05	0.05	6.456	8.4 (8,11)
17	0.05	1.00	0.05	0.05	4.428	15.6 (1,3)
18	0.30	0.75	0.15	0.20	9.702	1.7 (1,8)
19	1.00	1.00	0.75	1.00	6.744	1.5 (1,8)

Table 12
Relative probabilities of the models along the sequentially designed experiments in Example 3 with $Z = 0$

Run	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}	P_{13}
8	12.6	10.5	13.7	0.7	9.1	4.8	8.5	7.2	9.2	1.5	13.7	7.8	0.8
9	15.5	13.5	13.7	1.2	9.9	0.0	9.8	9.5	11.1	0.2	9.2	5.3	1.2
10	15.2	15.0	11.3	1.2	3.1	0.0	11.3	12.1	13.2	0.0	9.7	7.4	0.5
11	15.2	15.9	13.0	0.0	0.0	0.0	12.3	13.3	13.9	0.0	8.5	8.0	0.0
12	23.2	22.9	21.2	0.1	0.1	0.0	3.0	4.1	2.0	0.0	14.8	8.7	0.0
13	25.9	9.8	24.2	0.1	0.0	0.0	3.2	5.8	2.0	0.0	18.2	10.8	0.0
14	27.4	12.8	25.0	0.1	0.1	0.0	4.6	5.3	2.3	0.0	18.8	3.6	0.0
15	33.2	3.3	30.8	0.0	0.0	0.0	0.0	3.3	0.0	0.0	29.4	0.0	0.0
16	49.6	6.7	36.0	0.0	0.0	0.0	0.0	7.0	0.0	0.0	0.7	0.0	0.0
17	88.1	5.9	0.8	0.0	0.0	0.0	0.0	4.9	0.0	0.0	0.4	0.0	0.0
18	91.5	4.7	0.3	0.0	0.0	0.0	0.0	3.5	0.0	0.0	0.0	0.0	0.0
19	96.8	1.7	0.3	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0

Table 13
Sequentially designed experiments in Example 3 with $Z = 1$

Run	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r ($\times 10^3$)	R (m, n)
9	1.00	0.45	0.30	0.35	6.960	19.4 (3,5)
10	1.00	1.00	1.00	1.00	7.254	7.1 (9,11)
11	0.10	0.20	0.05	0.05	2.739	9.6 (2,11)
12	1.00	0.70	0.10	0.10	12.654	3.7 (11,12)
13	0.05	1.00	0.05	0.05	4.428	9.2 (3,11)
14	0.50	1.00	0.15	0.20	14.792	7.2 (1,11)
15	1.00	1.00	0.05	1.00	9.089	9.7 (1,7)
16	0.30	0.85	0.05	0.30	12.380	2.4 (1,8)

Table 14
Relative probabilities of the models along the sequentially designed experiments in Example 3 with $Z = 1$

Run	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}	P_{13}
8	12.6	10.5	13.7	0.7	9.1	4.8	8.5	7.2	9.2	1.5	13.7	7.8	0.8
9	12.4	13.1	14.2	0.0	0.0	2.0	11.0	10.1	10.8	0.2	16.2	9.9	0.0
10	18.7	19.5	22.2	0.0	0.1	0.3	2.4	2.2	0.8	0.0	23.5	10.1	0.0
11	22.7	6.2	24.8	0.0	0.1	0.5	3.9	3.7	0.8	0.0	23.8	13.5	0.0
12	25.5	7.6	27.1	0.0	0.1	0.8	5.9	5.6	0.0	0.0	27.4	0.0	0.0
13	26.3	8.4	23.7	0.0	0.0	0.0	7.3	7.1	0.0	0.0	27.2	0.0	0.0
14	55.1	10.5	7.9	0.0	0.0	0.0	14.2	11.2	0.0	0.0	1.1	0.0	0.0
15	68.9	10.3	9.1	0.0	0.0	0.0	0.0	11.4	0.0	0.0	0.3	0.0	0.0
16	99.6	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0

Table 15
Sequentially designed experiments in Example 3 with $Z = 5$

Run	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r ($\times 10^3$)	R (m, n)
9	0.05	1.00	0.15	0.10	3.367	4.8 (3,11)
10	0.05	0.30	0.05	0.05	3.673	3.0 (1,2)
11	1.00	1.00	1.00	1.00	7.254	9.1 (1,2)
12	1.00	0.15	0.05	0.05	2.438	1.8 (3,11)
13	0.40	0.80	0.10	0.05	14.466	2.7 (1,3)
14	1.00	1.00	0.35	0.20	14.588	3.5 (1,2)
15	0.30	0.80	0.05	1.00	4.882	14.7 (1,7)
16	1.00	1.00	0.40	1.00	7.417	1.5 (1,2)
17	0.30	0.70	0.10	0.30	10.386	1.6 (1,2)

Table 16
Relative probabilities of the models along the sequentially designed experiments in Example 3 with $Z = 5$

Run	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}	P_{13}
8	12.6	10.5	13.7	0.7	9.1	4.8	8.5	7.2	9.2	1.5	13.7	7.8	0.8
9	15.7	14.0	12	0.3	1.6	3.4	11.0	10.1	10.2	1.6	10.2	9.8	0.3
10	19.1	13.1	15.5	0.1	0.4	1.7	9.7	8.8	7.7	2.5	13.8	7.7	0.0
11	20.2	6.9	26.6	0.2	0.0	0.4	2.9	2.1	1.7	0.2	23.9	14.8	0.0
12	26.8	10.9	24.7	0.0	0.0	0.4	4.8	3.7	2.3	0.4	9.7	16.5	0.0
13	59.3	18.1	0.8	0.0	0.0	0.0	10.8	9.9	0.0	0.0	1.2	0.0	0.0
14	54.1	18.0	0.7	0.0	0.0	0.0	14.4	10.8	0.0	0.0	2.1	0.0	0.0
15	60.4	23.4	0.7	0.0	0.0	0.0	0.0	12.9	0.0	0.0	2.7	0.0	0.0
16	80.5	10.5	1.0	0.0	0.0	0.0	0.0	3.8	0.0	0.0	4.2	0.0	0.0
17	98.7	0.9	0.2	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0

As shown in Tables 11 and 12, 11 additional experiments are necessary for complete discrimination. Besides, it is important to observe that the designed experiments were at most times selected from a pair of models where one of the models presented a low relative probability level. This happened because the parameter Z is set to 0 and, in this case, the model probabilities did not affect the design of experiments. In order to concentrate efforts in discriminating among the most probable models, Z values of 1 and 5 are used. Table 13 shows the sequentially designed experiments when Z is equal to 1, while Table 14 shows the relative model probabilities as the experiments are executed.

When Z is made equal to 1, the first designed experiment is selected for discrimination between Models 3 and 5 (Table 13). However, when Z was set to 0, the first designed experiment was selected for discrimination between Models 5 and 6 (Table 11). Therefore, when Z is equal to 1, discrimination between Models 3 and 5 is preferred because the relative probability of Model 3 is higher than the relative probability of Model 6. After execution of this experiment Models 5 and 6 are discarded. After design and execution of the second experiment, the relative probabilities of Models 7–9 fall below the threshold value of 2.5%, but Models 7 and 8 are reconsidered in the procedure after of the third designed experiment. Model 11 has a high relative probability and five experiments were selected for discrimination of Model 11 from the others. But when one experiment is selected for discrimination between Model 1 and 11 (Experiment 14), Model 11 is discarded from the procedure, Model 1 assumes a high relative probability level and more two experiments are sufficient to complete the discrimination procedure, as expected, with Model 1 selected as the best one.

Tables 15 and 16 show the results obtained when Z is equal to 5. Observe that all designed experiments are selected for discrimination between the pair of models with higher relative probabilities.

When Z was set to 5 (or higher) all designed experiments were selected for discrimination between models with the highest probabilities. Seventeen experiments were necessary to indicate that Model 1 is the best one, one more than used in the case of Z equal to 1. Although the total number of experiments in the two cases are not very different, this certainly indicates that increasing Z beyond a certain limit does not cause any significant impact on the discrimination procedure, as experiments are performed to discriminate the models with the highest probabilities in all cases. As observed through many simulations, this practical limit is around the value of $Z = 2$.

Again the procedure proposed here is able to select the correct model among the initially proposed ones. It is also important to observe that this procedure apparently does not privilege the models with more adjustable parameters, since Model 8 has four parameters (the best one has five) and in all cases it were only discarded after execution of the last designed experiment.

In this example, the increase of parameter Z from 0 to 1 reduced the number of sequentially designed experiments, but

Table 17
Sequentially designed experiments in Example 4 with $Z = 0$

Run	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r ($\times 10^3$)	R (m, n)
9	0.05	1.00	0.05	0.65	2.165	35.6 (5,6)
10	0.45	0.90	0.05	1.00	7.676	19.1 (5,9)
11	1.00	0.20	1.00	0.10	2.224	3.2 (2,11)
12	0.65	1.00	1.00	1.00	6.222	5.6 (3,9)
13	0.80	1.00	0.15	0.60	11.614	4.0 (8,12)
14	1.00	0.60	0.05	0.20	10.481	3.6 (9,11)
15	0.05	0.25	0.05	0.05	2.903	3.1 (2,11)
16	0.25	0.45	0.05	0.05	8.372	3.8 (3,7)
17	1.00	0.40	0.05	0.05	8.956	4.9 (8,11)
18	0.65	1.00	0.15	0.25	13.684	4.5 (8,11)
19	0.10	1.00	1.00	0.05	2.112	5.9 (3,11)
20	1.00	1.00	0.45	0.15	12.425	2.8 (3,8)
21	0.25	0.90	0.05	0.20	13.113	2.9 (2,3)
22	1.00	0.15	0.05	0.05	2.543	3.1 (3,8)
23	0.05	1.00	0.05	0.05	4.110	3.3 (2,3)
24	1.00	0.15	0.05	0.05	4.101	3.3 (3,8)
25	0.05	0.25	0.05	0.05	1.765	1.1 (2,8)
26	1.00	1.00	0.10	0.05	17.632	3.0 (3,8)
27	0.05	0.25	0.05	0.05	–	0.4 (2,8)

Table 18
Relative probabilities of the models along the sequentially designed experiments in Example 4 with $Z = 0$

Run	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}	P_{13}
8	12.1	15.7	0.8	10.4	5.5	9.7	8.2	10.5	1.7	15.7	8.9	0.9
9	15.3	17.0	0.9	7.1	0.0	12.1	11.1	12.7	0.6	13.7	8.5	1.1
10	17.4	13.8	1.2	2.2	0.0	12.4	13.6	14.4	0.0	14.0	10.6	0.3
11	22.6	14.0	0.9	0.0	0.0	16.4	17.4	18.5	0.0	3.5	6.6	0.1
12	33.1	21.1	2.0	0.0	0.0	11.2	15.8	5.4	0.0	7.0	4.5	0.0
13	34.5	21.5	2.1	0.0	0.0	14.3	17.1	2.7	0.0	7.2	0.7	0.0
14	33.5	23.8	0.1	0.0	0.0	15.9	18.5	0.7	0.0	7.3	0.2	0.0
15	30.1	28.6	0.0	0.0	0.0	10.9	21.1	0.4	0.0	8.8	0.1	0.0
16	28.6	35.3	0.0	0.0	0.0	0.3	26.2	0.0	0.0	9.6	0.0	0.0
17	30.7	38.7	0.0	0.0	0.0	0.3	24.6	0.0	0.0	5.7	0.0	0.0
18	33.9	40.2	0.0	0.0	0.0	0.1	21.5	0.0	0.0	4.4	0.0	0.0
19	36.1	41.3	0.0	0.0	0.0	0.2	22.3	0.0	0.0	0.1	0.0	0.0
20	36.5	48.4	0.0	0.0	0.0	0.3	14.6	0.0	0.0	0.2	0.0	0.0
21	24.5	59.1	0.0	0.0	0.0	0.0	16.4	0.0	0.0	0.0	0.0	0.0
22	31.4	46.6	0.0	0.0	0.0	0.0	22.0	0.0	0.0	0.0	0.0	0.0
23	73.7	2.9	0.0	0.0	0.0	0.0	23.4	0.0	0.0	0.0	0.0	0.0
24	74.9	2.4	0.0	0.0	0.0	0.0	22.8	0.0	0.0	0.0	0.0	0.0
25	64.0	3.8	0.0	0.0	0.0	0.0	32.2	0.0	0.0	0.0	0.0	0.0
26	65.2	1.3	0.0	0.0	0.0	0.0	33.5	0.0	0.0	0.0	0.0	0.0

when Z was increased from 1 to 5, the number of experiments increased, showing that there is an optimal value of Z with respect to the number of experiments.

3.4. Example 4: water–gas shift reaction (in absence of the true model)

In all the three examples presented before, the model used to perform the simulations and generate the "experimental data" (the true model) was one of the analyzed rival models. In this forth example, discrimination among rival kinetic models for the WGSR is considered again, as described in the Example 3. However, although Model 1 is used to generate the "experimental data", it is not included in the set of plausible rival models. Therefore, the set of model candidates does not include the true model. The initial set of experiments used in this example was the same one used in Example 3 (Table 10). The Z parameter was allowed to assume the values 0, 1 and 5. Although Model 1 was excluded from the set of possible models, the nomenclature used to represent the models was the same one presented in Eqs. (23.a–m).

Tables 17 and 18 show the designed experiments and the relative model probabilities obtained when Z was set to 0.

Table 19
Sequentially designed experiments in Example 4 with $Z = 1$

Run	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r ($\times 10^3$)	R (m, n)
9	1.00	0.45	0.30	0.35	6.135	16.4 (3,5)
10	0.05	1.00	1.00	0.75	0.250	30.9 (3,6)
11	1.00	1.00	1.00	1.00	7.646	10.6 (9,11)
12	0.15	0.10	0.05	0.05	2.373	3.0 (2,3)
13	1.00	0.15	0.05	0.05	3.868	3.9 (2,11)
14	1.00	1.00	0.50	1.00	8.796	3.6 (3,7)
15	1.00	1.00	1.00	0.50	8.789	3.1 (3,8)
16	0.05	1.00	0.05	0.05	5.729	2.1 (3,11)
17	0.10	0.45	0.05	0.05	5.891	2.2 (2,3)
18	1.00	1.00	0.20	0.25	14.022	5.0 (3,8)
19	1.00	1.00	0.05	0.05	18.786	2.7 (2,3)
20	1.00	0.15	0.05	0.05	3.054	3.9 (2,3)
21	0.25	1.00	0.05	1.00	6.231	21.3 (2,7)
22	0.10	1.00	1.00	0.05	2.265	4.9 (2,11)
23	0.10	0.30	0.05	0.05	3.885	1.3 (2,8)
24	0.05	0.30	0.05	0.05	–	0.7 (2,8)

Table 20
Relative probabilities of the models along the sequentially designed experiments in Example 4 with $Z = 1$

Run	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}	P_{13}
8	12.1	15.7	0.8	10.4	5.5	9.7	8.2	10.5	1.7	15.7	8.9	0.9
9	14.8	17.3	0.0	0.0	4.5	11.7	10.3	12.2	0.6	17.7	11.0	0.0
10	19.8	22.4	0.0	0.0	0.0	13.7	12.0	13.6	0.0	14.8	3.6	0.0
11	31.7	30.0	0.0	0.1	0.0	7.4	6.8	3.9	0.0	13.2	6.9	0.0
12	17.8	34.6	0.0	0.1	0.0	8.1	7.9	3.9	0.0	17.9	9.6	0.0
13	18.3	39.9	0.0	0.0	0.0	8.5	9.0	3.7	0.0	9.0	11.7	0.0
14	20.3	38.0	0.0	0.0	0.0	3.5	10.5	4.2	0.0	10.9	12.6	0.0
15	18.6	37.5	0.0	0.0	0.0	4.7	5.7	5.2	0.0	13.6	14.7	0.0
16	23.7	42.3	0.0	0.0	0.0	3.6	8.5	0.0	0.0	18.7	3.3	0.0
17	24.5	45.0	0.0	0.0	0.0	3.0	9.4	0.0	0.0	17.5	0.7	0.0
18	33.0	31.0	0.0	0.0	0.0	4.5	12.0	0.0	0.0	19.5	0.0	0.0
19	38.5	18.8	0.0	0.0	0.0	3.3	16.5	0.0	0.0	22.9	0.0	0.0
20	50.3	4.6	0.0	0.0	0.0	5.3	23.5	0.0	0.0	16.4	0.0	0.0
21	51.6	4.7	0.0	0.0	0.0	0.0	25.6	0.0	0.0	18.1	0.0	0.0
22	57.8	6.3	0.0	0.0	0.0	0.0	31.2	0.0	0.0	4.7	0.0	0.0
23	54.6	6.5	0.0	0.0	0.0	0.0	33.7	0.0	0.0	5.2	0.0	0.0

After exclusion of Model 1 from the set of model candidates, the designed experiments (Table 17) became different from the ones presented in Example 3 (Table 11). After the execution of 18 designed experiments (run 26) only Models 2 and 3 presented relative probabilities higher than 2.5%. The sequential procedure was halted at this point because no further discrimination would be possible between these two models. It is interesting to observe that Models 2 and 8 were the last ones to be discarded in Example 3, when Z was set to 0.

The results obtained when Z is set to 1 are presented in Tables 19 and 20. These tables show that the sequential procedure is halted after 15 additional experiments (run 23) without discrimination among Models 2, 3, 8 and 11. The last designed experiment (run 24) is selected for discrimination between Models 2 and 8 (Table 19), which are the models with the highest relative probabilities. However, further discrimination is not possible because R becomes lower than 1. The results obtained when Z is set to 5 (Tables 21 and 22) are similar to the ones obtained when Z is set to 1 (Tables 19 and 20) and the sequential procedure is halted after 14 additional experiments without discrimination among Models 2, 3, 8 and 11.

In the last two cases, with Z set to 1 (Tables 19 and 20) and 5 (Tables 21 and 22), the number of remaining models at the end of the discrimination procedure was higher then observed in the case with Z set to 0 (Tables 17 and 18). Besides, the total number of designed experiments when Z is set to 0 was higher than in the other cases. When the Z value is set to 0, the relative model probabilities are not taken into consideration during the discrimination procedure and experiments are designed for discrimination between models that present low relative probabilities. This allows for fast elimination of these "bad" models. However, when Z is different from 0, models with low relative probabilities exert a minor impact on the discrimination

Table 21
Sequentially designed experiments in Example 4 with $Z = 5$

Run	p_{CO}	p_{H_2O}	p_{CO_2}	p_{H_2}	r ($\times 10^3$)	R (m, n)
9	0.05	1.00	0.15	0.10	4.443	2.5 (3,11)
10	0.05	0.30	0.05	0.05	3.266	3.4 (2,11)
11	0.35	1.00	0.35	1.00	6.735	4.5 (7,11)
12	1.00	1.00	0.90	0.45	8.964	5.0 (3,8)
13	0.05	1.00	1.00	1.00	0.103	4.0 (3,12)
14	1.00	0.50	0.10	0.05	10.785	2.0 (3,11)
15	0.20	1.00	0.10	0.10	12.467	1.9 (3,9)
16	1.00	1.00	0.20	0.20	15.397	2.9 (2,3)
17	1.00	0.15	0.05	0.05	4.449	3.9 (2,3)
18	1.00	0.15	0.05	0.05	2.991	3.0 (2,3)
19	0.10	0.50	0.05	0.05	6.345	2.3 (2,3)
20	1.00	0.10	0.50	0.50	1.747	2.7 (2,3)
21	0.15	0.95	0.05	1.00	4.471	8.1 (2,7)
22	1.00	0.10	0.50	0.50	0.113	2.7 (2,3)
23	0.05	0.30	0.05	0.05	–	0.3 (2,8)

Table 22
Relative probabilities of the models along the sequentially designed experiments in Example 4 with $Z = 5$

Run	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}	P_{11}	P_{12}	P_{13}
8	12.05	15.67	0.78	10.35	5.54	9.69	8.23	10.47	1.72	15.72	8.92	0.86
9	16.04	14.77	0.28	0.01	5.31	12.11	11.43	10.46	2.68	14.90	11.97	0.04
10	11.94	16.18	0.07	0.00	4.39	13.03	12.61	10.42	2.54	16.91	11.90	0.00
11	17.08	19.26	0.05	0.00	0.48	3.62	17.25	4.26	0.80	20.52	16.66	0.00
12	11.22	22.37	0.10	0.01	0.75	4.86	7.93	5.71	0.00	25.70	21.36	0.00
13	15.91	32.23	0.25	0.02	0.00	6.86	12.19	1.61	0.00	28.15	2.78	0.00
14	15.71	36.74	0.00	0.03	0.00	6.83	15.05	0.00	0.00	25.49	0.14	0.00
15	21.60	43.01	0.00	0.01	0.00	10.03	19.62	0.00	0.00	5.73	0.00	0.00
16	19.92	47.35	0.00	0.00	0.00	7.63	16.34	0.00	0.00	8.76	0.00	0.00
17	19.61	48.08	0.00	0.00	0.00	7.07	14.73	0.00	0.00	10.51	0.00	0.00
18	30.81	26.09	0.00	0.00	0.00	12.00	23.72	0.00	0.00	7.39	0.00	0.00
19	30.01	22.27	0.00	0.00	0.00	13.53	25.58	0.00	0.00	8.61	0.00	0.00
20	30.97	18.03	0.00	0.00	0.00	14.63	26.54	0.00	0.00	9.82	0.00	0.00
21	38.92	23.98	0.00	0.00	0.00	0.00	33.34	0.00	0.00	3.75	0.00	0.00
22	47.43	6.66	0.00	0.00	0.00	0.01	41.16	0.00	0.00	4.75	0.00	0.00

procedure. This allows for fast identification of discrimination problems, which explains the lower number of experiments in the last two sequences of experiments and, as a consequence, the higher number of model candidates at the end of the discrimination procedure. The interesting point here is to observe that the use of higher Z values lead to faster identification of discrimination problems and the absence of a best true model in the set of model candidates.

4. Conclusions

A new model discrimination procedure is proposed here, which makes use of the model probabilities based on the χ^2-distribution. It also makes use of Tsallis' concept of entropy, introducing the parameter Z that controls the degree of risk that the analyst is ready to accept. This procedure is an improved version of the one developed by Oliveira (1997) and used by Dariva et al. (1998).

Differently from Box and Hill's work, the discrimination procedure proposed herein does not depend on the particular sequence in which the experiments are executed. The relative probabilities of each model are calculated directly from the maximum likelihood estimator, which assembles all information to generate an approximate χ^2- statistic.

Large experimental and predictions variances are always of major concern. As clearly shown in Example 1, this effect becomes more critical whenever rival models have similar responses or many adjustable parameters. Nevertheless, other approaches are also limited by this fact.

Experimenter is prompted to review his experimental setup if the R-criterion fails. It is possible to overcome this drawback by extending the experimental region beyond its original bounds, or by refining the experimental technique in order to reduce the experimental error.

The Z-value gives flexibility to the procedure such that when the experimenter feels confident in the progress of the sequential design, fewer experiments will be necessary to confirm his results. On the other hand, a conservative position will delay the procedure until more information validates one particular model.

In all experimental problems analyzed in our group until now (Oliveira, 1997; Dariva et al., 1998 and this work), values of Z in the range $0 < Z < 5$ always led to similar conclusions. Therefore, it seems that the use of large Z values should be encouraged, as shown in Example 3 of this work. One should be aware, however, that conclusions could be made based on few experiments and the risk of these conclusions can be premature. Anyway, statistical tests can be always used to check the conclusions in each stage of the discrimination procedure.

Notation

D	value of design criteria
$D_{m,n}$	value of design criteria between models m and n
K, k	model parameters in Examples 1, 2 and 3
K_{eq}	equilibrium constant in Example 3
M	number of models in discrimination procedure
N	number of experimental data points
NP_m	number of parameters in model m
NY	number of response variables
p_m	probability density function defined by Eq. (6)
P_m	relative probability of model m defined by Eq. (16)
$P_{m,N}$	probability of model m after N experimental observations
r	kinetic rate in Example 3, $\text{mol g}^{-1}\,\text{s}^{-1}$
$R_{m,n}$	ratio between models divergence and prediction variances of model m and n
S	entropy defined by Eq. (3)
SS_m	sum of squares for model m defined by Eq. (14)
T	temperature, K
$\mathbf{V}$	variance–covariance matrix of experimental errors
$\mathbf{V}_m$	variance–covariance matrix of predictions by model m
$\mathbf{V}_{m,n}$	variance–covariance matrix defined by Eq. (12)
$\mathbf{x}$	vector of independent variables
$\hat{\mathbf{y}}_m$	vector of predictions by model m
Z	discrimination procedure parameter

Greek letters

α	significance level
β	approach to equilibrium, defined by Eq. (24)
σ^2	variance of experimental response
σ_m^2	variance of prediction by model m
υ	degrees of freedom
ϕ_m	model adequacy defined by Eq. (15)
χ^2	chi-square probability density function

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