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A model discrimination based approach to the determination of operating regimes for chemical reactors

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Abstract

The operation of a chemical process that involves the interplay between chemical reaction(s) and transport phenomena can materialise in the occurrence of a number of different operating regimes. When developing a new process, to achieve successful scale-up, the operating regime which yields ideal performance in smaller scale experiments should be identified and retained in the full scale realization. In the past, experimental procedures have been proposed for identifying operating regimes based on the *qualitative* trends of the response of a process to the change in operating conditions. In this work, a *quantitative* approach is proposed, in which the problem of determining operating regimes is formulated as one of model discrimination. The proposed approach makes use of hybrid models to handle missing mechanistic knowledge and an optimal experimental design technique was applied to generate the most discriminative data. A simulated case study on the nitration of toluene demonstrates that, compared with existing qualitative methods, this approach has the potential to achieve sharper discrimination, impose fewer requirements on experimental facilities, and complement existing methods.

Keywords: chemical reactor, operating regime, model discrimination, experimental design.

1. Introduction

The operation of a chemical process that involves the interplay between chemical reaction(s) and transport phenomena often materialises in the occurrence of a number of different operating regimes. When developing a new process, the operating regime which yields ideal performance (in terms of yield, selectivity, etc.) at a smaller scale should be identified and retained in the full scale realization, in order to achieve successful scale-up (Bourne, 2003). Since operating regimes often relate to different rate processes, a particular regime can be characterized in terms of a specific range for a dimensionless number which denotes the ratio of two characteristic times. However, it may not be possible to calculate such a dimensionless number when a new process is being developed since very little is known about the process at this stage, especially with respect to the chemical reaction kinetics. Previously it has been proposed that an experimental procedure specific to the type of process being investigated is adopted, to determine qualitatively the operating regimes. Furthermore, specific types of equipment such as constant interfacial area cells may be required to support the determination process (Atherton, 1993; Bourne, 2003).

In contrast to the existing qualitative approaches, this paper proposes a model-based quantitative approach for determining the operating regimes, based on the model discrimination technique. Model discrimination is a task whereby a limited number of appropriate models are selected from a larger number of candidate models (e.g. Kitrell, 1970; Stewart, et al, 1998; Jarosch et al, 2002). A typical approach is to fit all the candidate models using available experimental data and then assess the fitness of these candidate models according to a certain statistical criterion (Verheijin, 2003). To obtain the experimental data that realises the most efficient discrimination, optimal experimental design techniques can be applied (Atkinson & Denov, 1992).

The primary goal in this research is not to develop or identify the best model for a chemical process but to apply model discrimination as a tool to identify the true operating regime of a chemical process, where each candidate model represents one of the possible regimes. Since the knowledge about a process is incomplete during the early stages of process development, such a model is likely to be more "inexact" than those utilised, say, for the purpose of making predictions. However it is hypothesised that such models will be sufficient to enable differentiation between different operating regimes.

In Section 2, the proposed numerical approach to regime determination via model discrimination is presented. In Section 3, a case study on the process of toluene nitration is described and results and discussions are presented. Some concluding remarks are given in Section 4.

2. Determination of operating regime via model discrimination

The goal of optimal experimental design for model discrimination is to generate data that maximise the distance between candidate models. Since the distance between two models and that between a model and the data are dependent on the values of model parameters, a sequential procedure should be adopted which alternates between the estimation of parameters and the design/execution of the experiments. As the number of observations increases, the best model (with its associated parameterization) among the candidate models will approach the "true" model (Atkinson & Denov, 1992). This procedure requires to be customized in two aspects for the purpose of determining operating regimes.

The first aspect is the preparation of the candidate models. For the determination of the operating regime of a chemical process that involves the interplay of the chemical reaction and the transport phenomena, it is assumed, in this study, that the overall model structure reflecting conservations and the model of transport phenomena are available, but the knowledge about chemical reaction kinetics is incomplete, as may occur in practice. To allow for a candidate model to participate in the discrimination procedure, a black-box or grey-box approximation needs to be adopted to replace the missing mechanistic knowledge. Consequently, each candidate model is deemed to be hybrid, and it is the black-box part where the parameters are to be estimated in the parameter estimation stage.

The second aspect is the examination of the stopping criterion. A statistical test, Bartlett's chi-square test of homogeneity of variances (Verheijin, 2003), is applied to gradually eliminate the unfavourable models and to terminate the discrimination procedure when no more models can be eliminated. The statistic is defined as:

$$T = \frac{\sum_{m=1}^{M} (n - p_m) \ln(s_{tot}^2 / s_m^2)}{1 + \frac{1}{3(M-1)} \left[\sum_{m=1}^{M} \frac{1}{(n - p_m)} - \frac{1}{\sum_{m=1}^{M} (n - p_m)} \right]} \sim \chi^2_{M-1},$$

where M is the number of models, n is the total number of data points, s_m^2 is the residual sum of squares computed for model m, s_{tot}^2 is the average residual sum of squares of all models, and p_m is the number of parameters in model m. The hypothesis of homogeneous variances is rejected when the computed value of T is larger than the 95% quantile of the χ^2_{M-1} distribution. Applying the above customization defines the procedure actually adopted in this study, which is summarised in Figure 1.

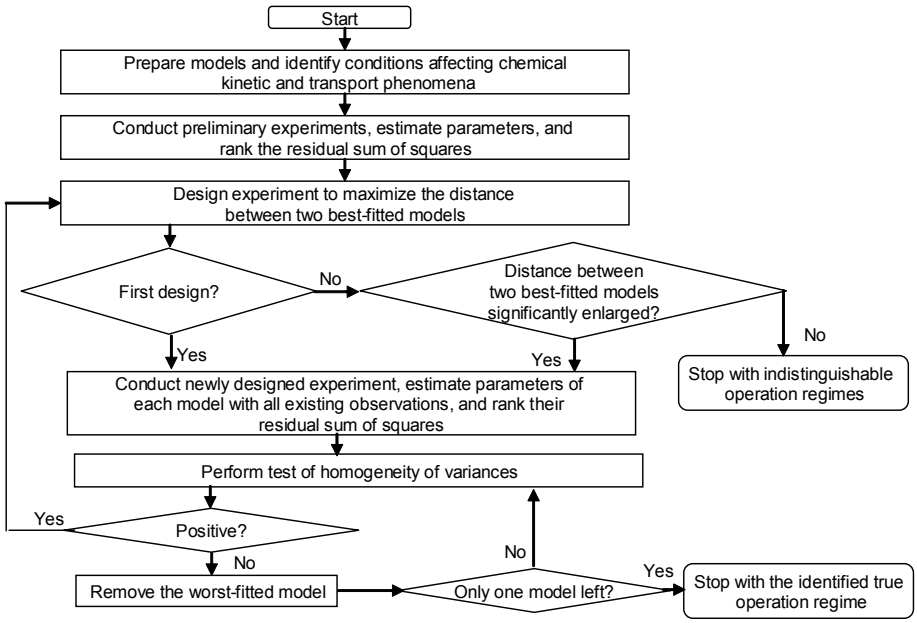

Figure 1. Procedure for operating regime determination via model discrimination.

3. Case study: Nitration of Toluene

Nitration of toluene is a liquid-liquid reaction process that takes place (as considered here) in a stirred batch reactor, which involves mass transfer between the organic phase and the aqueous phase. Depending on the operating conditions, the reactor may be operated under one of several regimes. In this case study, four regimes are considered, namely a *very slow reaction*, a *slow reaction*, a *slow-fast transition*, and a *fast reaction*. Detailed characterization and mathematical modelling of these regimes can be found in Bourne (2003), Doraiswamy & Sharma (1984), and Zaldivar, et al (1995&1996). The models are not presented here due to the space limitation but were implemented in gPROMS (PSE, 2004) to undertake dynamic simulations.

Under isothermal conditions, the apparent reaction rate constant of nitration, k, is a function of the composition of the mixed acid in which the nitration takes place. For the study of operating regime determination, the mechanistic model of k is assumed unknown, thus represents missing knowledge. For formulating the problem as one of model discrimination, a fourth-order polynomial black-box model was adopted for modelling k. This model was then used with the other parts of the model that corresponds to a specific operating regime, thereby forming a complete candidate model that was comparable with those representing other regimes.

The overall structure of the simulated study was such that (1) each of the four possible regimes was taken once to be the true one, resulting in four study groups (A-D); (2) for each group, the complete rigorous model corresponding to the true regime was used to generate the simulation data; (3) the person determining the operating regime would be unaware of which regime was the true one and thus perform the determination by discriminating between the four candidate models applying the strategy defined in Section 2 - this strategy was implemented in gPROMS; (4) the distance between two model candidates is computed by the time-integration of the difference between their predictions on the concentration of toluene in the organic phase during a batch; and (5) the operation condition used to increase the distance between candidate models was the concentration of H_2SO_4 in the mixed acid.

At the beginning of the study, each of the four groups was initiated by undertaking three preliminary (simulated) experiments to attain an initial estimate of the parameters of the black-box model. The discrimination procedure was then performed for each group and the results are shown in Table 1. The numbering of the models (*M*-) and the corresponding residual sums of squares (*S*-) are as follows: *very slow reaction - 1*, *slow reaction - 2*, *slow-to-fast transition - 3*, and *fast reaction - 4*. The ranges of the amount of H_2SO_4 (in *kg*) applicable to these operating regimes were set as: *Regime 1*: 0.4-0.6; *Regime 2*: 0.7 - 0.9; *Regime 3*: 1.3-1.5; *Regime 4*: 1.8-2.0.

Table 1. Results of operating regime determination via model discrimination

Group of test	True regime	Number of experiments	Ranking of the residual sum of squares	Results of Optimal Exp. Design		Remaining model(s) through Bartlett's Test
				Optimal amount of H_2SO_4 (kg)	Maximum Distance between two best fitted models	
A	1	3	S1(2.15)S2(2.75)S3(2.75) S4(11.5)	0.6	27.3	
		3+1	S1(2.18)S2(33.4) S3(33.6)S4(230)			M1
B	2	3	S4(1.54)S1(15.1) S3(29.6) S2(33.2)	0.9	3.71e3	
		3+1	S3(30.6)S2(34.4) S4(199)S1(9.28e3)	0.9	1.585	M2, M3
		3+2	S3(31.4)S2(35.4)	0.9	1.241	M2, M3
C	3	3	S3(7.81)S4(39.0) S1(236)S2(6.07e3)	1.3	6.00e2	
		3+1	S3(8.30)S4(1.45e3) S2(9.31e3) S1(4.30e4)			M3
D	4	3	S3(5.03)S4(6.66) S1(49.4)S2(7.84e4)	1.8	6.84e-2	
		3+1	S3(6.90)S4(6.88) S1(1.03e4) S2(1.68e5)	1.8	2.26e-2	M3, M4

The results of the case study demonstrate the advantages of the proposed method. If the slow-to-fast transition regime (No. 3) were not considered, the other three operating regimes would have been able to be successfully distinguished from one another and correctly identified as the true regime. It should be noted that no special requirement on the experimental equipment is imposed to obtain this result. In comparison, for the existing qualitative method for regime determination, the differentiation between the slow-reaction and the fast-reaction regimes requires the use of a constant interfacial area cell to maintain the interfacial area between the two phases (Atherton, 1993; Bourne, 2003). Additionally, the quantitative method has been able to correctly identify the transition regime as the true one. The handling of the transition regime by the existing qualitative method has not been reported, but it would be difficult for that method to distinguish between the slow reaction and the transition regime, whichever is the true regime, because their qualitative responses to a change in agitation and other conditions are similar.

There was one case (cf. Group D in Table 1) in which the proposed method failed but the existing qualitative method that makes use of a constant interfacial area cell may succeed. If such a reactor is used, it may be possible to exclusively identify the fast-reaction regime as the true regime by distinguishing it from the transition regime. This is because the transition regime is sensitive to a change in the phase volume ratio while the fast-reaction regime is not. The use of a constant interfacial area cell allows for separating the influence of the phase volume ratio from that of the interfacial area, and therefore makes the distinction between the two possible. This analysis suggests that, in this particular case, a constant interfacial area cell should be applied to cope with the difficulty faced by the proposed approach.

4. Concluding remarks

A quantitative approach to the determination of operating regimes based on model discrimination has been proposed, which is supported by techniques including hybrid modelling, optimal experimental design, and a statistical test to assess the homogeneity of the variances. A case study on a toluene nitration process demonstrated that, by leveraging mathematical models of possible operating regimes where black-box regressions are used to represent missing knowledge on chemical kinetics, the proposed approach has the potential to achieve sharper discrimination and require less experimental facilities in most cases. This is in contrast with existing qualitative methods where special experimental facilities are necessary.

There are two concerns pertaining to the effectiveness of the proposed approach. One is that the measurements of chemical process variables are often corrupted with noises. The result presented in the case study has not considered measurement errors which may make a difference on the estimate of the parameters of the black-box model, hence on the distances between different model candidates. However, a preliminary numerical study indicated that a major influence is most likely to occur only in the cases where the distance between the compared model candidates is insignificant, which are indeed also the cases where the proposed approach tends not to work well.

Another concern is that, whilst the reported case study has assumed an unknown expression for the reaction rate constant, in some other cases the entire chemical kinetics may be unclear (e.g. information such as the order of the reaction is not available at all). Under such a situation, this approach will still be applicable, simply by employing a black-box model to represent the entire chemical kinetics (i.e. one that

correlate the intrinsic reaction rate with the influential variables). A case study addressing this situation will be undertaken as future work.
This case study has shown particularly the difficulty of distinguishing the transition regime from its neighbours. It is suspected that the inter-model distance of these regimes might have been reduced due to the use of the black-box regression model embedded in every model being compared. This may contribute to the difficulties in the effective discrimination of these regimes. Research that addresses this issue is ongoing.

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