Chemical Engineering Science 104 (2013) 829–838

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Technologies comparison for iterative data acquisition strategies

Mathieu Florent [a,*], Commenge Jean-Marc [a], Falk Laurent [a], Lomel Sébastien [b]

[a] Laboratoire Réactions et Génie des Procédés, 1 rue Grandville, BP 20451, 54000 Nancy, France
[b] Solvay, Centre de Recherches et de Technologie de Lyon, 85 rue des Frères Perret, BP 62, 69192 Saint Fons Cedex, France

HIGHLIGHTS

- Data acquisition strategy takes into account several technologies.
- Intensified technologies are useful for data acquisition.
- Experimental windows and flexibility of sampling are specific for each technology.
- Unsteady state obtained by complex feed profile improves data acquisition.
- Flexibility of sampling enabled by plug-flow reactors improves data acquisition.

ARTICLE INFO

Article history:
Received 2 April 2013
Received in revised form
30 August 2013
Accepted 25 September 2013
Available online 15 October 2013

Keywords:
Intensification
Modeling
Experimental Strategy
Data acquisition
Parameter estimation

ABSTRACT

The present work proposes a new experimental strategy based on a general model which describes and includes different reactor technologies. The strategy is based on a sequential iterative approach where, in a predictive step, the model is used to propose optimal experimental conditions, and, in a validation step, experimental data are used to improve the parameter estimation.

A specific work bench with three types of reactors (batch, semi-batch stirred tank and continuous plug flow reactor) has been developed. The demonstration of the strategy is performed by using a classical parallel-consecutive reaction scheme, for which it has been demonstrated experimentally that the use of several reactors enlarges the experimental window, which enables to improve the accuracy on kinetic constants by comparison to using a restricted experimental window, with only one kind of reactor.

1. Introduction

Since a few years, intensified and microstructured reactors are an alternative to batch reactors. Thanks to their high heat and mass-transfer rates, a better control of operating conditions is possible leading to a better product quality (Falk et al., 2012; Hessel, 2009). However, it is difficult, time consuming and often expensive to quantitatively predict the real interest of intensified reactors and also to transpose a priori a batch process to a continuous process (Roberge et al., 2005). Appropriate strategies for design of experiments are therefore required to quantify the interests of these new technologies. One way is the use of phenomenological models to predict the performance of each technology.

The prediction quality of a phenomenological model mainly results from the good knowledge of heat and mass transfer as well as reaction kinetics. In other words, the more accurately heat and mass-transfers and reaction kinetics data are estimated, the more reliable is the model prediction. A method, firstly developed by Box and Lucas (1959), then improved several times (Hosten, 1974; Pritchard and Bacon, 1978; Franceschini and Macchietto, 2008), enables to make data acquisition as efficient as possible, by getting the best accuracy on parameters while minimizing the experimental effort. The present paper aims at demonstrating that taking into account several technologies is not only useful to improve process performance, which is already well established (Stankiewicz and Moulin, 2000), but can also be useful for data acquisition. Until now, publications on model-based experimental design only use one kind of reactor technology at once. For example, Issanchou et al. (2003) and Yang et al. (2006) used a batch reactor, Franceschini and Macchietto (2007) and Asprey and Macchietto (2000) a semi-batch, Schöneberger et al. (2009) a fixed-bed reactor and McMullen and Jensen (2011) used a Corning Advanced Flow Reactor. But the use of multiple technologies requires introducing the specificities of each technology in the acquisition strategy. Hence, for each technology, their operating windows, their ability to generate samples had been considered.

* Corresponding author. Tel.: +33 383175088.
E-mail address: florent.mathieu@univ-lorraine.fr (M. Florent).

0009-2509/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2013.09.053

For the sake of clarity, in this paper, a very simple experimental chemical system is used to illustrate this point. This chemical system is the synthesis of the 3-monoiodotyrosine. The objective is to compare the efficiency of a batch, a semi-batch, a plug-flow and a combination of them for data acquisition. In the experimental part of this study, only the kinetics aspects have been considered. Heat and mass transfer, nor temperature effects were included. To complete our experimental demonstration, presented in the first part of this paper, 'in-silico' experiments that enable to study very different chemical systems including heat and mass transfer issues are also presented at the end, to illustrate the capability of the method.

2. Methodology description

2.1. Formalism

To be applied, the data acquisition strategy requires the user to define a model that describes the system. Whatever the model used, it can be described thanks to the general following formalism:

$$\mathbf{y}_k = f(\boldsymbol{\xi}_k, \boldsymbol{\theta}) + \boldsymbol{\epsilon}_k \quad k \in \{1, \ldots, n_{sp}\} \tag{1}$$

- k is the measurement number among the n_{sp} the sampling points,
- $\boldsymbol{\xi}_k$ is the kth set of n_u experimental conditions of the $\boldsymbol{\Xi} = \{\boldsymbol{\xi}_1, \ldots, \boldsymbol{\xi}_k, \ldots, \boldsymbol{\xi}_{n_{sp}}\}$ set of n_{sp} samples,
- $\mathbf{y}_k$ is a set of n_{resp} measured responses obtained under the experimental conditions $\boldsymbol{\xi}_k$,
- $\boldsymbol{\theta}$ is a set of n_p parameters,
- f is an array function representing the model, also called model structure,
- $\boldsymbol{\epsilon}_k$ is a set of n_{resp} experimental errors obtained at the experimental conditions $\boldsymbol{\xi}_k$,
- $\boldsymbol{\Sigma}_{\mathbf{y}}$ is a $(n_{resp} \times n_{resp})$ the covariance matrix of the experimental error.

Once the model structure is defined by the user, the objective is to estimate the model parameters in order to match up observations to the model predictions. To perform the model fitting, the Maximum Likelihood Estimator is used, since the covariance matrix of the measured responses $\boldsymbol{\Sigma}_{\mathbf{y}}$ is supposed to be unknown. The criterion j to be minimized (Bates and Watts, 1988) is:

$$j(\boldsymbol{\theta}) = \ln \det \left\{ \sum_{k=1}^{n_{sp}} [\mathbf{y}_k - f(\boldsymbol{\xi}_k, \boldsymbol{\theta})][\mathbf{y}_k - f(\boldsymbol{\xi}_k, \boldsymbol{\theta})]^T \right\} \tag{2}$$

To compute the estimated parameters confidence interval a linear approximation is used. The $1-\alpha$ confidence interval for the mth parameter is then given by:

$$\hat{\theta}_m \pm t(n_{sp} - n_p; \alpha/2) \sqrt{\{\mathbf{V}\}_{mm}} \tag{3}$$

where t is the student distribution, and $\mathbf{V}$ the covariance matrix of the parameters, which is approximated by using the Fisher matrix (Franceschini and Macchietto, 2008). The covariance matrix of measured responses $\hat{\boldsymbol{\Sigma}}_{\mathbf{y}}$, required to compute the Fisher matrix, is estimated using Eq. (4):

$$\hat{\boldsymbol{\Sigma}}_{\mathbf{y}} = \frac{1}{n_{sp}} \sum_{k=1}^{n_{pm}} [\mathbf{y}_k - f(\boldsymbol{\xi}_k, \boldsymbol{\theta})][\mathbf{y}_k - f(\boldsymbol{\xi}_k, \boldsymbol{\theta})]^T \tag{4}$$

The objective of the data acquisition strategy proposed by Box and Lucas (1959) is to find which next experiment minimizes the volume of the confidence region. By making a linear approximation, which implies that the confidence region is an ellipsoid, the confidence region can be minimized by minimizing the determinant of the covariance matrix of the parameters $\mathbf{V}$. This optimal design criterion is called 'D-optimality'. Other optimal design critera exist, such as the E-optimality that minimizes the longest axis of the confidence ellipsoid or the A-optimality that minimizes the volume of the enclosing box around the confidence region, but they will not be used in this paper. The data acquisition strategy is then an iterative procedure which is illustrated in Fig. 1.

Designing experiments when using various technologies requires defining the concept of "one experiment". An experiment is defined here as a set of several sampling points (denoted $\boldsymbol{\Xi}$) that are generated with the same technology within a reasonable time spent at lab, which must be roughly the same for each technology. Of course, 'reasonable' is an arbitrary concept which depends on the studied chemical system. For each technology, we considered its specificity, defined by its experimental window and its ability to generate samples.

2.2. Experimental window

The experimental window of a reactor is defined by:

- **Intrinsic limitations**. Each technology has its own operating conditions, as illustrated in Fig. 2, which compares a classical batch stirred tank with a continuous plug-flow reactor. For example, a glass stirred reactor operating under atmospheric pressure is limited in working temperature by the solvent boiling temperature, whereas a continuous pressurized reactor, such as a microchannel reactor, enables to work at much higher pressure and temperature. As well, these two reactors operate under different residence times: stirred reactors can be operated from few minutes to many hours while microchannel reactors can only achieve few seconds of residence time.

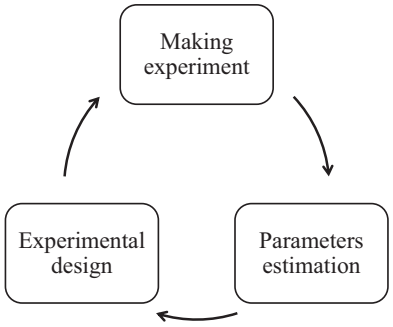

Fig. 1. Illustration of the iterative procedure for data acquisition.

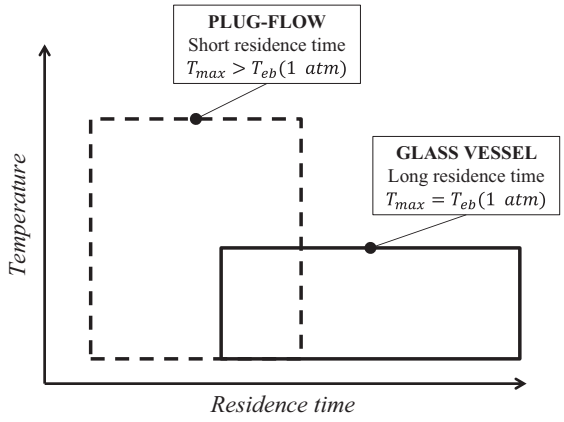

Fig. 2. Example of different experimental windows for two typical reactors.