Validation of a model for a biodiesel production process through model-based experiment design for parameter precision

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Abstract

Advanced model-based experiment design techniques are a reliable tool for rapid development, refining and validation of process models. When dealing with complex reaction networks, the current techniques show convergence problems if one tries to plan a set of experiments for the estimation of all the parameters. In a previous work (Franceschini & Macchietto 2005), a methodology to overcome this problem had been proposed and described through the application to a case study (a biodiesel production process). The aim of this paper is to present the results of the parameter estimation, which was carried out using the data collected under the optimally designed experimental conditions. In the light of these results, the procedure proposed for the experiment design will be assessed in term of advantages and limitations, and possible solutions to overcome the problems will be mentioned. Regarding the case study, the model was almost completely validated in just one iteration of the experiment design procedure and was then used for an optimisation study, the results of which will be presented here in order to identify the effect of the most important operating variables on the process yield.

Keywords: Biodiesel, Kinetics Elucidation, Model-based Experiment design, Nonlinear Systems, Parameter estimation, Process Optimisation

1. INTRODUCTION

Dynamic mechanistic modelling has become a key activity in process engineering: its main advantage is the possibility of gaining a better understanding of the different phenomena which occur within the system under investigation. Therefore, building high quality and validated models of process systems has become a step not to be ignored for many applications such as model-based product and process design, control and optimisation. By expressing the underlying phenomena in a mathematical form, these detailed models can be used to improve product, process and plant performances in a wide range of applications. On the other hand, collecting the data which are required to build and validate a model can be costly, both in terms of money and time. Therefore, there is a need to develop these models in a systematic way in order to maximise the information obtainable from each experiment and to minimise the number of analyses, the cost of materials and the time required.

When building these models, one uses a priori knowledge such as physical, chemical or biological laws to propose one or more possible models. These laws dictate the model structure and such models invariably contain adjustable parameters that may have physical meaning. Typically, one desires to establish if it is at all possible to determine their values. If so, the next step is to estimate the parameters with the maximum precision and to validate their values and the model statistically. This second aspect involves adequacy tests for the model (i.e. how well the model explains the observed data) and tests to check whether or not a parameter is well determined in the model (t-test) (Asprey 1999). For the statistical verification of detailed dynamic models, Asprey and Macchietto (2000) have presented a systematic model-building procedure. This approach is an iterative method which involves:

- ✓ proposing a mathematical parametric model
- ✓ designing optimal experiments using the model;
- ✓ estimating the model parameters using the experimental data collected under the optimally planned conditions;
- ✓ checking for model adequacy.

The whole procedure must be repeated until a satisfactory degree of precision in the model predictions is achieved.

A key step within this approach is the design of experiments so as to obtain the maximum information from the experimental apparatus being modelled. In particular, model-based experiment design aims at assisting a modeller/experimenter in devising experiments that will yield the most informative data, in a statistical sense, for use in parameter estimation and model validation. In mathematical terms, given an initial model and assumed parameters, the aim is to minimise the expected inference region of the parameters, i.e. to make the elements of the parameters variance-covariance matrix small. An experiment design calculation thus involves minimising some metrics of this matrix by choosing a set of experiment decision variables (length, time-varying and time invariant controls, initial conditions, sampling times, etc.) subject to equality or inequality constraints (Asprey & Macchietto 2000). Various real-valued functions have been suggested as metrics for the parameters variance-covariance matrix (Asprey & Macchietto 2002). The most common criteria are four:

1. D-optimality which minimises the determinant of the covariance matrix and thus the volume of the joint confidence region;
2. E-optimality which minimises the largest eigenvalue of the covariance matrix and thus the size of the major axis of the joint confidence region;
3. A-optimality which minimises the trace of the covariance matrix and thus the dimensions of the enclosing box around the joint confidence region;
4. Modified E-optimality which minimises the condition number of the covariance matrix (i.e. the ratio between the maximum and minimum eigenvalue) and thus makes the joint confidence region as spherical as possible (Versyck et al. 1997).

For a detailed discussion of these criteria, reference is made to Walter and Pronzato (1990).

Despite the importance of the problem, there has been a relatively modest amount of work in the past on the application of experiment design techniques to dynamic systems. The concepts and some results were presented in the late 1980's and early 1990's for general mechanistic models consisting of differential and algebraic equations (Espie 1986; Espie & Macchietto 1988; Zullo 1991). More recent work on the application of these techniques has been reported by Körkel *et al*. (2004), Bauer *et al.* (2000) and Versyck *et al.* (1997, 1998), who applied these methods to investigate the unstructured growth kinetics in biological systems. A series of studies carried out recently by Asprey *et al.* (1999, 2000, 2002) has significantly improved the methodology and allowed the inclusion of a routine for experiment design for parameter precision in a commercially available software package as gPROMS (Process System Enterprise Ltd.) (Process System Enterprise 2004).

1.1 Objectives and structure of this paper

We applied these experiment design techniques to a model describing a case study of practical interest: a biodiesel production process. The aim was to identify the parameters of the kinetic network with the maximum precision and thus validate the model. This case study was chosen on purpose because was very suitable for the application of the methodology which we wanted to develop. Our objective was to delineate an experiment design problem appropriate for complex kinetic networks (in the biodiesel case there are three consecutive and competitive reactions). When dealing with these types of kinetic schemes, usually the high number of parameters, the correlations between them and the form of the equations involved (such as Arrhenius' equations) create convergence problems if one tries to plan a set of experiments for the estimation of all the parameters of the network. In order to overcome this problem, in a previous paper (Franceschini & Macchietto 2005) we had proposed a solution, which will be briefly described in section 1.2. This solution requires the planning of experiments for the estimation of individual, couples or groups of parameters with the others fixed at their current values and uses sensitivity analysis to identify which parameters can be estimated with the data collected from a single optimal experiment.

After the planning of the required optimal experiments and the subsequent data collection in our laboratory, a last step remained to be tackled in order to validate the model: the estimation of the parameters using the new data. In a model building procedure, such as that formalised by Asprey and Macchietto (2000), parameter estimation is a stage which logically follows the experiment design calculations and the experimental work. This paper deals with the problems and the results of this essential step.
It is also worthy to note that, only after the parameter estimation, the procedure which we had proposed for the experiment design could be assessed and some conclusions about its efficiency could be drawn. Thus, the aims of this paper were three:

- ✓ to highlight problems which can occur in the parameter estimation of highly nonlinear systems, such as those which make use of Arrhenius' equations, and to describe the solution proposed;
- ✓ to present the results of the parameter estimation for the purpose of model validation
- ✓ and to use these results as evidence of the advantages and of the problems that have still to be solved in our methodology.

Regarding the structure of this paper, the next section contains a brief summary of the work previously carried out. This is essential to understand what will follow. Then, section 2 describes the procedure adopted for the parameter estimation. This was performed in two steps: an individual estimation of the parameters according to the results of the experiment design (see section 2.1) and a global estimation of all the parameters together (see section 2.2). Section 2.3 contains a discussion about the validity of the methodology adopted for the experiment design. In the end, an application of the validated model is presented in section 3, which reports the results of a preliminary optimisation study. This was carried out to investigate the effect of the most important operating variables on the yield of the system.

1.2 Background

Biodiesel would be an ideal substitute for the conventional diesel fuel if only it was more competitive economically. Efforts have been made to reduce its cost by optimising its production processes. The subject of our study is one of these processes: the transesterification of a vegetable oil (rapeseed oil) with methanol in presence of an alkali catalyst (sodium methoxide) under mild pressure conditions in a batch reactor is. A previous experimental work was carried out in 2002 in order to maximise the conversion of this process (Lemieuvre 2002). Then, the experimental results of this study were used by Franceschini (2003) in order to build a mathematical model which reproduces the physical behaviour of this system. The estimation of the kinetic parameters involved in the model proved to be difficult and problematic: only the equilibrium constants could be estimated. Simulations results showed that a larger number of more informative data were required in order to enable a better estimation of the kinetic parameters (Franceschini *et al.* 2004). Almost all the data, which were collected in the previous study, were concentrated in the region controlled by the equilibrium and, therefore, contained no useful information on the dynamics of the system. Consequently, new data were necessary and experiment design is an adequate technique to obtain as informative data as possible.

The model developed by Franceschini (2003) uses the kinetic scheme proposed by Noureddini and Zhu in 1997. According to these authors, the reaction consists of three consecutive and reversible steps:

$$\begin{aligned} &\mathrm{TG} + \mathrm{M} \xleftrightarrow{k_1,k_2} \mathrm{DG} + \mathrm{E} \\ &\mathrm{DG} + \mathrm{M} \xleftrightarrow{k_3,k_4} \mathrm{MG} + \mathrm{E} \\ &\mathrm{MG} + \mathrm{M} \xleftrightarrow{k_5,k_6} \mathrm{G} + \mathrm{E} \end{aligned} \tag{1}$$

where TG, DG and MG are, respectively, the tri-, di- and mono-glycerides and M, G and E indicate methanol, glycerol and the mixture of methyl esters which form biodiesel. The model described in detail most of the phenomena which occur in the experimental reactor (for example phase equilibrium, temperature varying with time, methanol evaporation, energy input and losses) and only the kinetic parameters were not known; the values provided in Noureddini & Zhu (1997) were used.

Modelling, simulation, parameter estimation and experiment design were all carried out using gPROMS (Process System Enterprise 2004), interfaced with two databases, Infodata and DIPPR (AIChE 2004), and a program, Multiflash (Infochem Computer 2004), for the calculation of the thermo-physical properties of the reaction mixture.

1.2.1 Experiment design problem

The results of the calculations of a model-based experiment design problem allow a set of new optimal experiments to be planned. In our case, however, we wanted to carry out these experiments with the available experimental and analytical setup. The goal was to investigate the potentialities of the methodology even in experimental conditions which are not the best. This led to an interesting experiment design problem, which coupled a complex reaction network (three consecutive and competitive reversible reactions) with many practical constraints and limitations of the apparatus, such as, for example, the non-isothermal conditions. Non-isothermal experiments are not optimal for kinetic studies and complicate the mathematical resolution of the problem because of the use of Arrhenius' equations. All these restrictions and the high number of parameters to be estimated did not allow a set of experiments for the global estimation of all the parameters to be designed. The only realizable solution was to plan experiments for the estimation of individual, couples or groups of parameters (not more than three parameters, otherwise convergence problems occurred) with the others fixed at their current values. The criterion chosen to group parameters was to try to plan a single experiment for those parameters which showed the maximum of the normalised sensitivity in the same time interval. Advantages and limitations of this approach will be discussed in section 2.3 after the presentation of the parameter estimation results.

Table 1 reports the experimental conditions of the six optimally designed experiments, which were performed in our laboratory in order to collect the data required for the parameter estimation.

Table 1. Optimal experimental conditions for the estimation of the transesterification parameters

	EXP.G	EXP.H	EXP.I	EXP.L	EXP.M	EXP.N
Parameters estimated	A_1	A_2 & A_6	A_3 & A_4	A_5	E_1,E_3 & E_5	E_2,E_4 & E_6
Process time (min)	19	94	71	64	27	76
T max (K)	310	368	340	332	316	341
Amount of oil/ MeOH (mol/l)	3/23.76	3/14.57	3.28/16.96	3.18/14.98	3.95/12	3.95/12
Number of samples	8	12	8	14	8	8
Variables measured	E	E	E	E	MG, E	G, E
Number of analyses (EP+GP)	8+8	12+12	8+8	14+14	8+8	8+8
Precision (t-value)	36.59	13.4/8.5	9.64/5.2	24.89	96/76/49	12.6/21/52
Reference t-value	1.895	1.812	1.943	1.771	1.771	1.771

2. PARAMETER ESTIMATION

The parameter estimation was carried out in two steps. The first stage was an individual estimation: the parameters were estimated singly or in pairs or in groups of three (depending on how they had been coupled during the experiment design), using the data only of the specifically designed experiment and with the other parameters fixed at their current values. Then, a global estimation was performed using the data of all the optimal experiments and the values found in the previous step as starting points. The problems which emerged and the solution proposed to overcome them will be described in section 2.2.

2.1 Individual estimations

According to the experiment design results, it was possible to estimate all the parameters with enough precision, although the t-test results were almost always less than the predicted ones (compare the second and third column of Table 3). This is due to the fact that the values of the variance used during the experiment design study for the three measured variables were too small. A standard value of 0.5 was adopted for all the variables due to lack of knowledge about the real experimental errors correlated with the analytical procedures.

In all the estimations, the constant variance model ($\sigma^2 = \omega^2$) was used. In order to check the validity of this assumption, some attempts were carried out with the more complex heteroscedastic model for the variances of the measured variables. This model can be expressed as:

$$\sigma^2 = \omega^2 \cdot (z^2 + \varepsilon)^{\gamma} \tag{2}$$

where *z* is the measured value and ε is a very small but non-zero number calculated by the solver. This ensures that the variance has a meaningful definition for measured values that are equal to zero or very small. When this model was used in the estimations, the value of γ calculated by gPROMS was always equal to zero. This means that the heteroscedastic variance model reduced to its respective constant variance model.

The initial guesses of ω for the three responses in the constant variance model were assumed equal to the variances experimentally measured. Since these variances took into account only the experimental errors of the analyses, the upper bounds for ω were imposed a little higher in order to consider the errors in the reproducibility of the experiments as well. These errors were not experimentally measured.

Table 2 shows the results obtained for the twelve parameters involved in the model. The table reports the final value (FV) of each parameter together with the 95% confidence interval (CI) and the initial guess (IG), the lower (LB) and upper bound (UB). The last two columns contain the initial and final value of the objective functions (OF), which were minimised in each estimation.

Table 2. Results of the individual parameter estimations

Parameter	FV	95% CI	IG	LB	UB	OF (initial value)	OF (final value)
A_1	0.0353	0.003912	0.2157	0.01	1	5733.88	13.51
A_2	0.01121	0.001924	0.00312	0.0001	0.1	700.644	22.93
A_3	3098	1003	33320	1000	10^5	1284.96	11.68
A_4	1291	508.2	77.92	0.1	10^4	1284.96	14.22
A_5	0.003338	0.0005788	0.002933	0.0001	0.01	116.089	33.66
A_6	0.005371	0.002097	0.009905	0.0001	0.1	700.644	22.93
E_1	4814	840.3	5892	1000	12000	36390.9	45.73
E_2	4303	658.5	4269	1000	12000	1152.6	41.85
E_3	9032	100.5	9280	3000	15000	36390.9	45.73
E_4	6769	108	6760	1000	15000	1152.6	41.85
E_5	4271	73.34	3995	1000	10000	36390.9	45.73
E_6	5328	125.8	5532	1000	12000	1152.6	41.85

In order to check the reliability of the estimation, two statistical tests are automatically performed by gPROMS (Process System Enterprise 2004b). The t-test is used to establish the statistical significance of the estimation: the t-value shows the percentage accuracy of the estimated parameters with respect to the 95% confidence intervals. The test is satisfied when the calculated value is larger than the reference t-value. The χ^2 test concerns the goodness of the fit and is verified when the weighted residual is less than the 95% reference χ^2-value. Table 3 reports the results of the tests performed for each parameter and, as we can see, both tests were always satisfied.

Table 3. Results of the statistical tests for the individual estimations (the third column contains the t-values as predicted by the experiment design calculations)

Parameter	95% t-value	95% Predicted t-value	Reference t-value (95%)	Weighted residual	χ^2value (95%)
A_1	9.023	36.59	1.943	8	12.592
A_2	5.826	13.4	1.833	12	16.919
A_3	3.087	9.64	2.132	6	9.488
A_4	2.541	5.2	2.015	9.085	11.07
A_5	5.767	24.89	1.771	20.82	22.362
A_6	2.561	8.5	1.833	12	16.919
E_1	5.728	96	1.706	33.971	38.885
E_2	6.535	12.6	1.708	32	37.652
E_3	89.9	76	1.706	33.971	38.885
E_4	62.7	21	1.708	32	37.652
E_5	73.34	49	1.706	33.971	38.885
E_6	42.37	52	1.708	32	37.652

2.2 Global estimation

The individual estimations confirmed the results which were expected from the experiment design; the values found from these calculations were then used as starting points for a global estimation of all the parameters. The data of all the optimal experiments were employed.

The first results obtained revealed high correlations between the parameters. These correlations made the convergence problematic and prevented the parameters from being properly identified (the t-tests showed inadequate values). The cause of these problems was sought in the mathematical formulation of the model. It is well known that a model with the Arrhenius' law directly incorporated can make the estimation of the parameters very hard because of the high correlation between pre-exponential factors and corresponding activation energies. In order to overcome this problem, three different solutions were tried:

- ✓ a re-parameterisation of the model using a reference temperature (Asprey & Naka 1999),
- ✓ a re-parameterisation of the model by means of an approximation of the exponential function with a power function
- ✓ and a linearization of the Arrhenius' equations.

The first solution required the Arrhenius' equation to be replaced with the following expression:

$$k_j = A_j^* \cdot \exp\left[\left(\frac{-E_j}{R}\right) \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{3}$$

where

$$A_j^* = A_j \cdot \exp\left(\frac{-E_j}{RT_{ref}}\right) \tag{4}$$

and T_{ref} is a mean reference temperature. This solution proved to be inadequate. Although efficient to overcome the correlation problem, this re-parameterisation generated a new difficulty: the scaling problem became significant and the convergence was hindered again. In this case study, the pre-exponential factors were much smaller than the activation energies because of the units of measurement used in the model (the pre-exponential factors were expressed in $m^3/(mol \cdot s)$). The application of the re-parameterisation made the difference between the values of the parameters E_j and A_j^* larger and, therefore, the mathematical solution of the problem was not helped at all.

The second solution required the exponential function to be approximated with a power function:

$$\exp\left(\frac{-E_j}{R \cdot T}\right) \approx b \cdot T^c \tag{5}$$

where b and c are parameters which can be found by fitting the exponential curves. The Arrhenius' equation was therefore replaced with the following expression:

$$k_j = A_j^* \cdot T^c \tag{6}$$

where

$$A_j^* = A_j \cdot b\,. \tag{7}$$

This solution proved to be satisfactory: an estimation of the parameters A_j^* and c was found with enough precision for most of the parameters. The only drawback of this approach is the impossibility to go back, after the estimation, to the values of the original parameters.

The last solution simply required the Arrhenius' equation to be replaced with the following linear equation:

$$\cos t_j = A_j^* - E_j / T \tag{8}$$

where

$$A_j^* = \ln(A_j) \tag{9}$$

and

$$k_j = \exp(\mathrm{cos\,t}_j)\ . \tag{10}$$

This was the approach chosen for the global estimation.

Despite the use of this linearization or of the re-parameterisation of the second approach, the global estimation of the twelve parameters still showed some difficulties. So the estimation was carried out in two steps: first, only the pre-exponential factors (A_j^*) were estimated with the activation energies fixed at their initial values. Then, the activation energies were estimated with the pre-exponential factors fixed at the values found in the previous step. A third iteration was not necessary because no further improvements were obtained with a re-estimation of all the parameters together using the values found in the previous two steps as starting points.

The global estimation here described was carried out using the data of all the optimal experiments except Exp.G (see Table 1). This choice needs to be justified. A recent experimental work, carried out in our group, showed that the initial mixing of the two liquid phases, where the reactants are at the beginning of the transesterification, took up to two minutes for small volumes such as 50-90 ml. We can, therefore, expect a longer time to be required to obtain a good mixing of four or more litres of reaction mixture. When the experiment design study was performed, this information was not available and, therefore, one minute was chosen as the minimum time for the first sampling point. Exp.G required all its data to be collected in the first 18 minutes of the reaction. Therefore, we preferred to discard these data because we could not be sure that dishomogeneities in the mixing could have affected them.

Table 4 shows the results of the global estimation and the values of the statistical tests. We can see from the χ^2 tests that the fits were always adequate (this means that the model was able to reproduce the experimental data). Figure 1 shows the goodness of the fit graphically.

Table 4. Results of the global parameter estimation

Parameter	Final value	95% confidence interval	95% t-value	Reference t-value (95%)	Weighted residual	χ^2value (95%)
A_1^*	0.4865	54.75	$4.529 \cdot 10^{-2}$	1.69	45.333	49.802
A_2^*	-6.961	518.6	$1.995 \cdot 10^{-2}$			
A_3^*	9.6362	0.9103	10.59			
A_4^*	2.7263	1.598	1.706			
A_5^*	-6.88	0.4594	14.98			
A_6^*	-3.861	0.5313	7.267			
E_1	5447	$2.75 \cdot 10^{5}$	$1.982 \cdot 10^{-2}$	1.68	58.345	60.481
E_2	4947	$7.73 \cdot 10^{5}$	$6.405 \cdot 10^{-3}$			
E_3	9296	293.2	31.7			
E_4	6792	872.6	7.783			
E_5	3994	187.7	21.28			
E_6	5487	346	15.86			

Eight parameters out of twelve were identified with enough precision as shown by the t-tests results and by the confidence intervals in Table 4. The parameters of the first reaction step (A_1, A_2, E_1 and E_2) were not statistically validated. This could have been caused by two different problems: correlation and lack of data for the first minutes of the reaction. Sometimes in multi-parameter models, a t-value may be low because of the high correlations between parameters. From the correlation matrix results (not shown here), a high correlation between the corresponding parameters (A_1 with E_1 and A_2 with E_2) can be noticed, as can be also seen from the confidence ellipsoids in Figure 2.

Regarding the second problem, the data which were collected in the first minutes of the reaction were discarded for the reason above-mentioned. Unfortunately, as shown from the sensitivity analysis, the model is particularly sensitive to parameters A_1 and E_1 exactly at the beginning of the process, where no sure data could be collected. We can therefore conclude that, with the available experimental apparatus, the proper identification of these parameters can be really difficult. One possible solution could be to use a higher mixing rate at the beginning of the process to shorten the time required to obtain a homogenous phase. However, this hypothesis must be verified with some additional experiments before proceeding with another experiment design aimed at planning experiments for the estimation of these four parameters.

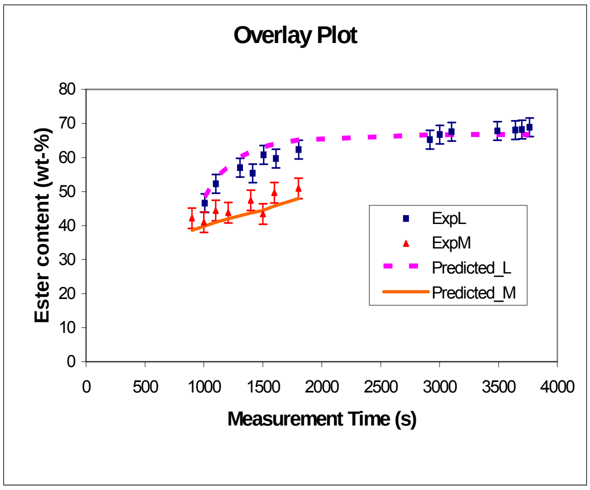

Figure 1a. Comparison between experimental data and simulated profiles for the ester content of Exp.L and Exp.M

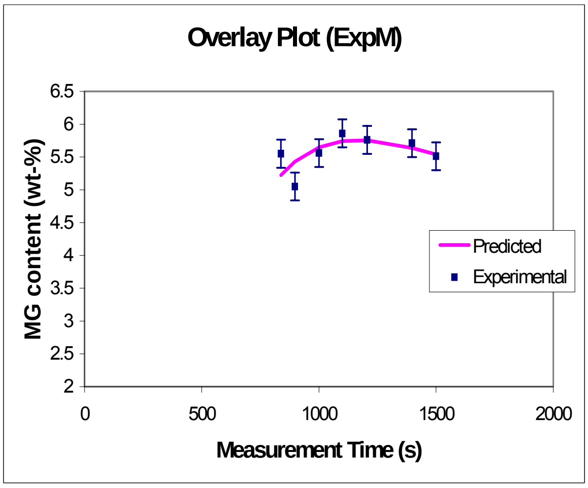

Figure 1b. Comparison between experimental data and simulated profiles for the monoglycerides content of Exp.M

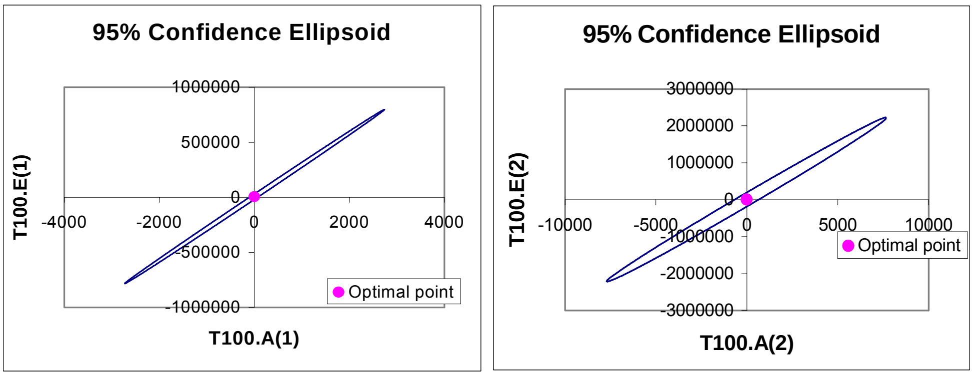

Figure 2. 95% confidence ellipsoids for two pairs of corresponding parameters (A_1 with E_1 and A_2 with E_2)

2.3 Discussion

From the comparison between the final values of the parameters obtained with the individual estimations (Table 2) and with the global estimation (Table 4), it can be seen that almost all of the parameters (except A_5 and A_6) show very different values. This is a clear indication that interactions between parameters are significant.

It is possible now to extract some conclusions from all this work. The approach proposed for the experiment design (to plan experiments for the estimation of groups of parameters with the others fixed at their current values) has been demonstrated valid but requires further developments. Its main advantage is the capability to deal with complex reaction networks: the currently available experiment design techniques are affected by convergence problems when the number of parameters is high and there are correlations between them. In most of the cases, no experiments can be planned in these situations (our biodiesel case is an example). Nevertheless, there is a limitation in the procedure proposed: the significant correlations between the parameters are neglected during the planning of the experiments but their effect appears during the estimation and makes the identification of the parameters more difficult. Therefore, the current experiment design technique must be modified to overcome this drawback of the procedure and this is under investigation at the moment.

A short explanation of the basic ideas of this improvement is given here. At the moment, experiment design is aimed at optimising the information content of the experiments. For example, regarding the sampling points, the method tries to collect them in the time interval around the maximum of the curve of the normalised sensitivity. Only the sensitivity of the responses to the parameters under investigation (i.e. the parameters for which the new experiment is going to be planned) is taken into account. The technique does not consider the effect of the other parameters in this interval. It is possible (as we have seen in the previous sections) that the experiment planned for the estimation of one parameter is highly influenced by the values of the other parameters and this will emerge only during the estimation. Therefore, the method can be improved so as to take into account not only the sensitivity of the responses to the parameters under investigation but also to all the other parameters of the model. In other words, regarding the previous example, data should be collected only when the sensitivity is high respect to the parameter/s under consideration and low respect to the others. This could lead to the identification of intervals for the data collection where the normalised sensitivity has not its maximum value, but should permit a better decoupling between the parameters than the current technique. Therefore, a trade off will have to be found between information content of the experiments and parameter decoupling.

3. OPTIMISATION STUDY

Although four of the model parameters were still not statistically identified after the first iteration of the experiment design strategy, the partially validated model was used for a preliminary optimisation study. A deep investigation of the influence of the various operating conditions on the process yield was the main aim of this study. In the next experimental work, which we are going to plan, some of the optimised experiments, here presented, will be performed. The objective will be to verify experimentally if the predictions of the model are or not correct. In this way, it will be possible to have an idea of the significance of the four parameters, which are still not statistically validated, and to decide on the necessity of another experiment design study for the identification of these parameters.

The influence of four important operating conditions was analysed in a series of dynamic optimisations:

1. the process time,

2. the reaction temperature profile,
3. the molar ratio between methanol and oil
4. and the flow rate of the methanol feed (semi-batch charge).

The combined effects of these variables were taken into account as well. The gPROMS optimisation routine (Process System Enterprise 2004b) was used to perform these studies with a tolerance for the optimiser of 10^{-6} (the tolerance for the solver of the DAE equations system was set at 10^{-10}). Finally, the objective function to be maximised was the ester yield calculated with respect to the limited reagent: the oil.

3.1 Process time effect

The reaction time effect was studied with a constant molar ratio between alcohol and oil, a 3 to 1 ratio (the stochiometric one). The cases T and T1, shown in Table 5, are suitable to illustrate the influence of the process time on the ester yield, because the only differences between them were the initial guess and the upper bound for the process time (respectively 115 and 167 minutes for the first case versus 65 and 117 for the second one). We can see that no observable effect is obtained on the objective function by doubling the process duration. In case T1, the equilibrium was reached with steeper temperature slopes (this was a consequence of the optimiser effort to maximise the objective function in a shorter time), whereas, in case T, a temperature profile with more moderate increases was used. Both cases gave the same results.

3.2 Temperature effect

The temperature effect was studied with a constant molar ratio between alcohol and oil, a 3 to 1 ratio (the stochiometric one). The reaction is globally exothermic; therefore, an upper limit (see the fourth column of Table 5) had to be imposed in order to avoid an excessive rise in the temperature. Although higher temperatures would probably have led to higher yields, they were not investigated for two reasons. First, the necessary heating would have become too expensive. Second, the loss of methanol, in terms of molecules not any more available for the reaction, would have become too important because of the increase in the evaporation. Two variables were optimised: the temperature profile (modelled as a piecewise linear control) and the process time (PT). The results of all the significant runs are shown in Table 5 and will be now discussed.

Table 5. Temperature and time effect (UB is the upper bound)

Case	UB for PT (min,sec)	PT (min, sec)	UB for T (K)	Final T (K)	Initial profile for T	Final yield
T	166’40”	130’58”	400	400	Yes	65.50%
T1	116’40”	57’07”	400	400	Yes	65.50%
T3	116’40”	71’08”	340	340	Yes	63.65%
T4	116’40”	58’48”	380	380	Yes	65.81%
T8	116’40”	84’41’	380	380	No	66.18%

Regarding the temperature effect, the results of cases T1 and T4 can be compared (they have a similar process time, so the difference in the objective function value is caused only by the difference in the temperature). We can see that, if we lower the upper limit for the temperature from 400 K (case T1) to 380 K (case T4), the loss in the ester yield is about 0.7%. A rise in the final temperature from 340 K (case T3) to 380 K (case T4) causes an increase in the objective function of about 2.2%. We can, therefore, conclude that the temperature increase has a positive effect on the ester yield, but this impact tends to zero after a certain threshold (~380 K in this case). This could be expected because the global reaction is only slightly exothermic and, therefore, the temperature effect alone can not be sufficient to improve the process significantly.

All the runs, except case T8, were carried out giving an initial profile for the temperature to the optimiser in order to help the solution process. The results of case T8 were achieved without the use of an initial profile and we can see that the yield obtained is the highest. The resultant temperature profile is, however, not realizable in practise because in the last step requires an increase in the temperature of about 0.7 °C/s, which is too high for the heating system available in our reactor. Nevertheless, it is interesting to note that only such a steep increase in the temperature of the final interval of the process can improve the yield further. This sheer rise in the temperature of the last step can be observed in almost all of the runs performed (even with different molar ratios between methanol and oil). However, when an initial temperature profile is given to the optimiser, the slopes obtained are always feasible.

All the comments reported in this section were confirmed by the studies carried out with different molar ratios between the reactants and, so, can be considered independent from this other important variable.

3.3 Molar ratio effect

In order to study the effect of the methanol excess on the process yield, the optimisations described above were repeated using three different molar ratios (in the initial charge) between alcohol and oil (4:1, 5:1, 6:1). Higher ratios were not investigated because a too large amount of unreacted methanol makes the final separation too difficult. The results are shown in Table 6. A molar ratio of 6:1 and a final temperature of 378 K allow a final yield of about 86% to be obtained in just hour, with also a significant improvement in the batch productivity (compared to the other cases). When the initial amount of methanol was added as an additional operating variable to be optimised (last row in Table 6), the same optimal molar ratio and the same final temperature were obtained. In this case, only the initial amount of oil was fixed during the optimisation. Therefore, the optimal value of the initial moles of methanol, found after the convergence, allowed the optimal molar ratio between the reactants to be calculated. An upper limit for the initial moles of methanol was imposed in order not to exceed the maximum 6:1 ratio between alcohol and oil.

Table 6. Molar ratio effect

MR	Process time (min,sec)	Final T (K)	Final yield	Productivity $kg_{ester}/(kg_{oil\ feed}\cdot h)$
3:1	58’48”	380	65.81%	0.675
4:1	58’20”	380	75.24%	0.77
5:1	82’17”	380	81.56%	0.60
6:1	57’08”	378	85.78%	0.906
6:1 (Opt)	75’19”	377.6	85.78%	0.69

These results are in agreement with the findings of the previous study (Franceschini *et al.* 2004), where an optimal molar ratio of 6:1 and a final temperature of 360 K allowed the maximum yield to be obtained in just one hour.

3.4 The methanol injection effect (fed-batch operation)

This variable was studied with the amount of methanol initially charged in the reactor (M_0) fixed at two different values: equal to 3.8 mol (which corresponds to an alcohol/oil molar ratio of 1:1) in the first case and almost null in the second one. The remaining methanol was fed with an optimised flow rate (see Figure 3a). Table 7 shows the results which were obtained. In the last case reported in the table, the initial amount of methanol (M_0) was an additional variable to be optimised.

Table 7. Methanol injection effect

Case	M_0 (mol)	Process time (min,sec)	T (K)	Final yield	Productivity $kg_{ester}/(kg_{oil\ feed}\cdot h)$
1	3.8	67'55"	See Fig. 3b	85.71%	0.77
2	0.1	72'54"	See Fig. 3b	85.80%	0.71
3	0.101 (Opt.)	64'57"	See Fig.3b	85.79%	0.814

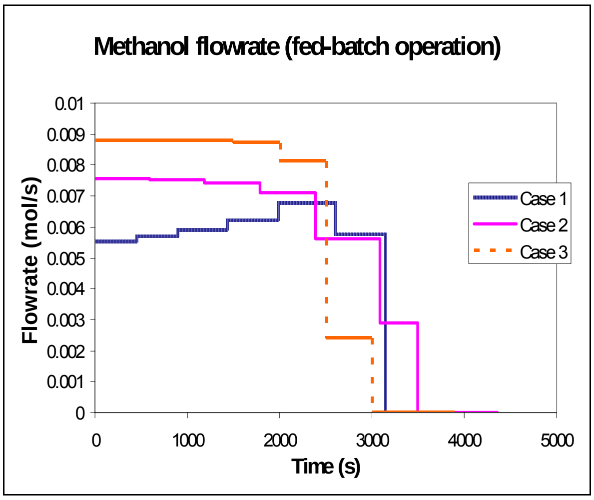

Figure 3a. Optimal flow rate profiles for the three cases of Table 7

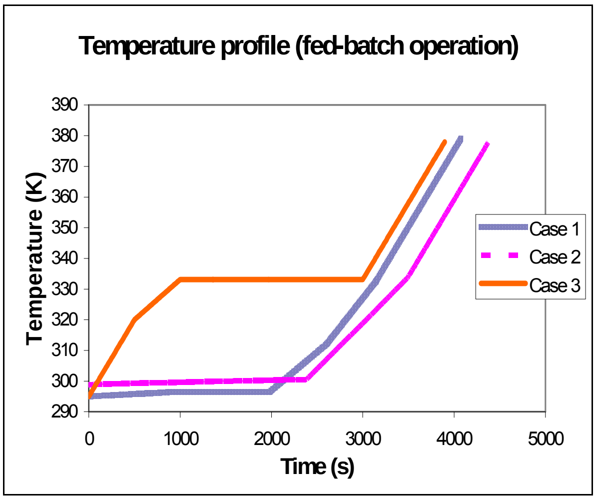

Figure 3b. Optimal temperature profiles for the three cases of Table 7

In order to avoid an excessive methanol charge in the reactor, some limits for the volume of the liquid mixture and for the alcohol amount were imposed. For example, the maximum allowed amount of methanol in the reactor corresponds again to a 6:1 alcohol/oil molar ratio. Since the initial amount of oil was fixed at 3.8 mol, methanol charged in the reactor at the beginning (M_0) plus methanol fed with the optimised flow rate could not exceed 22.8 mol.

The results are similar to the findings of the previous section for what concerns the process yield; in all the cases, the maximum allowed alcohol excess was used and almost the maximum temperature was reached. Therefore, no significant differences could be obtained in the process yield by modifying the feeding policy: batch or fed-batch operations gave the same results.

However, if the fed-batch operation is chosen, the results show that it is better to charge all methanol during the process according to the optimised flow rate (case 2) than to charge some methanol at the beginning and then to start with the fed-batch operation (case 1). Case 3 is a confirmation of this fact: if the initial amount of methanol is added as an additional variable to be optimised (as in case 3), the optimised value found by gPROMS for M_0 is the minimum amount allowed (0.1 and not zero in order to avoid numerical problems).

These results contrast in part with the findings of the previous study (Franceschini *et al.* 2004), where the fed-batch operation was shown to need a longer reaction time with a very remarkable worsening of the productivity (three times lower). In both cases the fed-batch operation was demonstrated not to improve the reaction yield significantly. In this study, there is still a lengthening of the reaction time (but more moderate) probably due to the feeding of methanol, which delays the reaching of the equilibrium. The remarkable worsening of the productivity observed in the previous study was probably caused by the dynamic behaviour of the system not being well modelled with the experimental data available at that moment. This problem has been dealt with in this study using an experiment design approach as described in the previous sections.

4. CONCLUSIONS

Experiment design techniques are a powerful tool to reduce the amount of experimental work required for model validation. An intelligent use of these methods allows the experiments with the maximum information content to be selected. The application of these techniques usually requires an iterative procedure, in particular if the initial values of the parameters are far from the true ones. In this paper, model-based experiment design has been applied to a model describing a biodiesel production process in order to identify the parameters of its complex kinetic network (three consecutive and competitive reactions). The high number of parameters and the form of the equations involved (Arrhenius' equations) generated convergence problems when we tried to design a set of experiments for the estimation of all the parameters of the network. The solution proposed in a previous paper (Franceschini & Macchietto 2005) requires the planning of experiments for the estimations of individual, couples or groups of parameters with the others fixed at their current values and uses sensitivity analysis to identify which parameters can be estimated with the data collected from a single optimal experiment. As demonstrated in this paper, the approach proposed is valid but requires further developments because does not take into account the correlations between the parameters and this creates problems during the subsequent global estimation. A different formulation of the objective function or some modifications of the experiment design algorithms will be necessary to solve this problem and this is the subject of our current and future work.

However, using the procedure proposed, it was possible to validate the model almost completely in just one single iteration. Only the parameters of the first reaction step were not identified successfully (from a statistical point of view). Data in the first reaction minutes are required to estimate these parameters properly. The reactor used was demonstrated not to be the best apparatus to collect data in the initial part of the reaction because of the mixing difficulties explained in section 2.2. Therefore, it should be probably better to investigate the use of other types of reactor before planning the second iteration of the experiment design.

An optimisation study was performed using the new model (even if it was not completely validated) in order to investigate the influence of the various operating conditions on the process yield. It emerged that the amount of methanol is the variable which must be modified in order to achieve higher yields. The effect of the temperature is less significant and the fed-batch operation does not improve the process yield compared to a batch charge of methanol. A molar ratio of 6:1 and a final temperature of 378 K allow a final yield of about 86% to be obtained in just hour, with also a significant improvement in the batch productivity.

Current work involves the improvement of our new experiment design procedure and the planning of some new experiments in order to investigate the mixing effect and, as mentioned above, check the model predictions.

REFERENCES

AIChE 2004, *DIPPR: Data compilation of pure compound properties*, Design Institute for Physical Properties.

Asprey, S. P. 1999, *Parameter estimation and optimal experimental design in multi-response non-linear dynamic situations: a progress report.*, Imperial College London.

Asprey, S. P. & Macchietto, S. 2000, "Statistical tools for optimal dynamic model building", *Computers & Chemical Engineering*, vol. 24, no. 2-7, pp. 1261-1267.

Asprey, S. P. & Macchietto, S. 2002, "Designing robust optimal dynamic experiments", *Journal of Process Control*, vol. 12, no. 4, pp. 545-556.

Asprey, S. P. & Naka, Y. 1999, "Mathematical problems in fitting kinetic models - Some new perspectives", *Journal of Chemical Engineering of Japan*, vol. 32, no. 3, pp. 328-337.

Bauer, I., Bock, G., Körkel, S. & Schlöder, J. P. 2000, "Numerical methods for optimum experimental design in DAE systems", *Journal of Computational and Applied Mathematics*, vol. 120, no. 1-2, pp. 1-25.

Espie, D. M. 1986, *The use of nonlinear parameter estimation for dynamic chemical reactor modelling,* PhD Thesis, University of London.

Espie, D. M. & Macchietto, S. 1988, "Nonlinear Transformations for Parameter-Estimation", *Industrial & Engineering Chemistry Research*, vol. 27, no. 11, pp. 2175-2179.

Franceschini, G. 2003, *Biodiesel da transesterificazione di olio vegetale: modellazione matematica ed analisi numerica del processo,* Tesi di laurea, University of Padua, Italy.

Franceschini, G., Bertucco, A. & Macchietto, S. "Simulation and optimisation of a biodiesel production process", *Proceedings of the Convegno GRICU 2004: Nuove Frontiere di Applicazione delle Metodologie dell'Ingegneria Chimica*, Porto d'Ischia (Napoli), Italy 12-15 September, pp. 667-670.

Franceschini, G. & Macchietto, S. 2005, “A numerical experiment design study on a biodiesel production process”, *Proceedings of the 2005 European Symposium on Computer Aided Chemical Engineering-15 (ESCAPE-15)*, Barcelona, Spain 29 May-1 June, pp. 349-354.

Infochem Computer 2004, *Multiflash v.3.0, Multiflash Command Reference*, Infochem Computer services Ltd., London.

Körkel, S., Kostina, E., Bock, H. G. & Schlöder, J. P. 2004, "Numerical methods for optimal control problems in design of robust optimal experiments for nonlinear dynamic processes", *Optimization Methods and Software*, vol. 19, no. 3-4, pp. 327-338.

Lemieuvre, M. 2002, *Biodiesel process study: experiments and simulations,* MSc Thesis, Imperial College, London.

Noureddini, H. & Zhu, D. 1997, "Kinetics of Transesterification of Soybean Oil", *Journal of the American Oil Chemist's society (JAOCS)*, vol. 74, pp. 1457-1463.

Process System Enterprise 2004a, *gPROMS v.2.3.0, Experiment Design for Parameter Precision in gPROMS*, Process System Enterprise Ltd, London.

Process System Enterprise 2004b, *gPROMS v.2.3.0, Introductory and Advanced User Guide*, Process System Enterprise Ltd, London.

Versyck, K. J., Claes, J. E. & Van Impe, J. F. 1998, "Optimal experimental design for practical identification of unstructured growth models", *Mathematics and Computers in Simulation*, vol. 46, no. 5-6, pp. 621-629.

Versyck, K. J. & Van Impe, J. F. 1998, "Trade-offs in design of fed-batch experiments for optimal estimation of biokinetic parameters", *Proceedings of the 1998 IEEE International Conference on Control applications*, Trieste, Italy 1- 4 September, pp. 51-55.

Versyck, K. J., Claes, J. E. & Van Impe, J. F. 1997, "Practical identification of unstructured growth kinetics by application of optimal experimental design", *Biotechnology Progress*, vol. 13, no. 5, pp. 524-531.

Walter, E. & Pronzato, L. 1990, "Qualitative and Quantitative Experiment Design for Phenomenological Models - A Survey", *Automatica*, vol. 26, no. 2, pp. 195-213.

Zullo, L. 1991, *Computer aided design of experiments. An engineering approach,* PhD Thesis, University of London.