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Sequential Experimental Design for Precise Parameter Estimation. 1. Use of Reparameterization

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An important problem in chemical reaction engineering is the estimation of the parameters of a kinetic model from experimental data. Available procedures for precise parameter estimation are reviewed, and it is shown that the precision of the parameters is reduced if they are strongly correlated and the experimental data are noisy, even if the powerful statistical technique of sequential experimental design is employed. This work shows that the sequential experimental design can be used more effectively to reduce these problems if it is coupled with a reparameterized model. Better parameter estimates can be obtained with a more economical experimental program, even in the presence of significant experimental noise. Further, a natural criterion, expressed in terms of the number of function evaluations required to compute the optimal design, emerges as a means of terminating the sequential experimental design program.

Introduction

In reaction rate modeling, a high correlation is often encountered between the estimates of preexponential factor (A_0) and the activation energy (E) of the Arrhenius expression for a rate constant k

$$k = A_0 \exp(-E/RT) \tag{1}$$

This high correlation complicates matters when the estimates are to be used in mechanistic interpretation or in reactor design, especially when extrapolation beyond measured temperatures is needed.

A reduction in the correlation between A_0 and E of eq 1 can be achieved by reparameterization, originally suggested by Box (1960) and since recommended by others (Draper and Smith, 1966; Mezaki and Kittrell, 1967; Pritchard and Bacon, 1975)

$$k = k^* \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{2}$$

where

$$k^* \doteq A_0 \exp(-E/RT^*) \tag{3}$$

and T^* is a reference temperature. While the use of this reparameterized (RP) model is undoubtedly successful in parameter estimation, its effect on the design of experiments to provide the data has not received any attention.

In this paper experimental design criteria where the objective of the experiments is to estimate parameters in a given model are briefly reviewed. The influence of reparameterization on designs and on the accuracy and convergence of the parameter estimates is then demonstrated for various experimental error levels.

Design Criterion for Parameter Estimation

Consider a rate model given by

$$y_u = f(\mathbf{X}_u,\mathbf{K}) + \epsilon_u \tag{4}$$

where y_u is the measured reaction rate; $\mathbf{X}_u = (x_{1u}, x_{2u}, ..., x_{mu})$ are the m operating variables for experimental run u, $u = 1, 2, ..., n$; and $\mathbf{K} = (k_1, k_2, ..., k_p)^T$ are the p parameters. If the random errors ϵ_u, $u = 1, 2, ..., n$ are independently and normally distributed with constant variance σ^2, then the variance-covariance matrix of the least square parameter estimates $\hat{\mathbf{K}}$ is

$$\mathbf{V} = (\mathbf{D}^T\mathbf{D})^{-1}\sigma^2 \tag{5}$$

where $\mathbf{D}$ is an $(n \times p)$ matrix. An element of $\mathbf{D}$, d_{uj} is the partial derivative with respect to the jth parameter evaluated for the uth experimental conditions of $\mathbf{X}_u$ at the least-squares estimates $\mathbf{K} = \hat{\mathbf{K}}$

$$d_{uj} = \left[\frac{\partial f(\mathbf{X}_u, \mathbf{K})}{\partial \mathbf{K}_j}\right]_{\mathbf{K} = \hat{\mathbf{K}}} \tag{6}$$

Box and Lucas (1959) have shown that the choice of ex-

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Table I. Order of Magnitude Comparison of "True" Parameter Values

non-RP model		RP model	
parameter	value	parameter	value
A_0	4.629×10^3	θ	−8.8222
E	1.160×10^4	ϕ	8.672
α	0.33	α	0.33
β	1.0	β	1.0

perimental variables, $\mathbf{X}_u$, which will minimize the determinant

$$|(\mathbf{D}^T\mathbf{D})^{-1}| \tag{7}$$

or, equivalently maximize the determinant

$$|\mathbf{D}^T\mathbf{D}| \tag{8}$$

will also minimize the volume of the joint confidence region of the parameter estimates. The square root of the determinant (8) is in fact inversely proportional to the volume of the joint confidence region of the estimates.

Box and Lucas (1959) dealt with the simultaneous planning of exactly as many experiments as there are parameters in the model. Later, Box and Hunter (1965) established a criterion, generally known as the minimum volume design criterion, for a sequential design whereby all available experimental results are analyzed each time an additional experiment has been performed, and the current information is then used for the design of the next experiment by maximizing the determinant (8). Box and Hunter indicated that this strategy not only minimises the size of the confidence region of the parameter estimates but also the correlation between them. Some applications of this criterion to real experimental studies in the field of chemical kinetics have been reported by Mezaki (1969), Froment and Mezaki (1970), and Graham and Stevenson (1972).

Two new design criteria, the shape design criterion (Hosten, 1974) and the correlation design criterion (Pritchard and Bacon, 1978), both of which reduced the correlation in estimates, have recently been proposed. However, these criteria fail to reduce the correlation between A_0 and E in the Arrhenius expression, and the sizes of the joint confidence regions obtained by these two criteria were substantially higher than that obtained with minimum volume design criterion. A comparison study of these three criteria is reported by Agarwal and Brisk (1985).

Example

The ethylene hydrogenation reaction system studied by Barton (1976) has been used to investigate the influence of reparameterization of a rate law on both sequential experimental design and parameter estimation, in the presence of strongly correlated parameters and noisy experimental data. The hydrogenation of ethylene was investigated over supported nickel catalyst at atmospheric pressure in a differential reactor. The rate model for the reaction was

$$\text{model 1:} \quad r_{C_2H_6} = A_0 \exp(-E/RT) X^{\alpha}_{C_2H_4} X^{\beta}_{H_2} \tag{9}$$

where $r_{C_2H_6}$ is the rate of formation of ethane and $X_{C_2H_4}$ and X_{H_2} are the mole fractions of ethylene and hydrogen, respectively. After incorporating the reparameterized eq 2, rate model 1 becomes

$$r_{C_2H_6} = k^* \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] X^{\alpha}_{C_2H_4} X^{\beta}_{H_2} \tag{10}$$

To ensure a nonnegative preexponential factor and activation energy, transformations suggested by Box (1966) were also incorporated. The final rate model is written as

$$\text{model 2:} \quad r_{C_2H_6} = \exp(\theta) \exp(-T' \exp(\phi)) X^{\alpha}_{C_2H_4} X^{\beta}_{H_2} \tag{11}$$

where

$$T' = 1/T - 1/T^* \tag{12}$$

$$\exp(\theta) = k^* \tag{13}$$

and

$$\exp(\phi) = E/R \tag{14}$$

Model 1 and model 2 were used to examine the effect of reparameterization on the precision of the parameter estimates when utilizing the minimum volume design criterion in sequential experimental design.

The original parameter estimates, hereafter referred to as the "true" values, were taken from Barton's analysis and are given in Table I. The values for θ and ϕ were calculated on the basis of an average temperature of 338 K (Table I).

An initial set of six experiments was planned so as to span the range of variables in a fairly arbitrary way. This set was used to initiate the simulated design programs. The continuous operating region chosen was defined by $X_{C_2H_4}$ from 0.1 to 0.4, X_{H_2} from 0.4 to 0.8, and T from 313 to 363 K. Constraints from the actual experiments were used to bound the allowable space. Thus an upper limit for the reaction rate was set at 1.5×10^{-4} kg-mol/(s kg of cat.) because higher reaction rates gave runaway conditions (Barton, 1976). The mole fraction was restricted by $X_{C_2H_4} + X_{H_2} < 1.0$, with nitrogen used as a diluent when necessary. The experimental programs were terminated after 24 experiments.

The data from each set of experiments consisted of one set of independent variables (mole fractions of ethylene and hydrogen and reaction temperature) together with the dependent variable obtained by adding errors to the true values calculated from eq 9 or 11. The errors used were calculated from

$$\%\ \text{error} = \text{random number} \times \%\ \text{noise}$$

The random numbers were generated from a Gaussian normal distribution with zero mean and a constant standard deviation of 0.5. The noise levels were 10% and 40%.

Results and Discussion

Table II shows the initial block of six experiments and subsequent simulated experiments for models 1 and 2. As expected, the designs led to somewhat different experimental conditions except for the first few experiments.

The parameters A_0 and E for model 1 and their recalculated values for model 2 which were estimated after each simulated experiment in sequence for each of two noise levels are shown in Figures 1 and 2. It is seen that both parameters are slightly better estimated by using the RP model (model 2) for 10% noise and much better estimated for 40% noise. It is also evident that for both models at low noise the parameters converge to the true values after a few experiments. At the higher noise level the parameter estimates in the non-RP model (model 1) show some instability and do not necessarily approach the true values. In fact, in Figure 1, the values of A_0 from the non-RP model with 40% noise level are completely off scale after the eighth experiment. In the RP model, however, the parameters converge toward the expected values.

This convergence or lack of convergence could be interpreted by postulating that at low noise the surface of the experimental design criterion as a function of operating

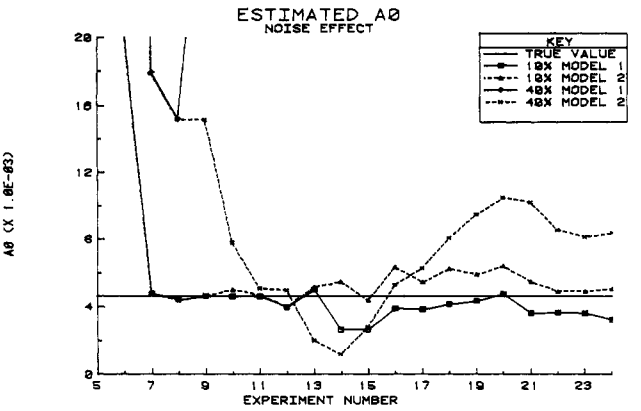

Figure 1. Estimated preexponential factor (A_0) vs. experiment number.

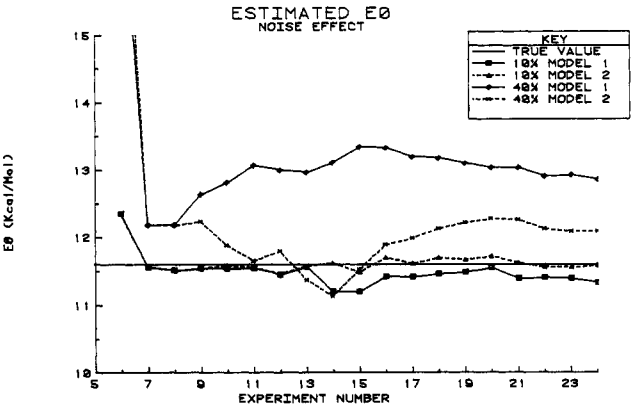

Figure 2. Estimated activation energy (E) vs. experiment number.

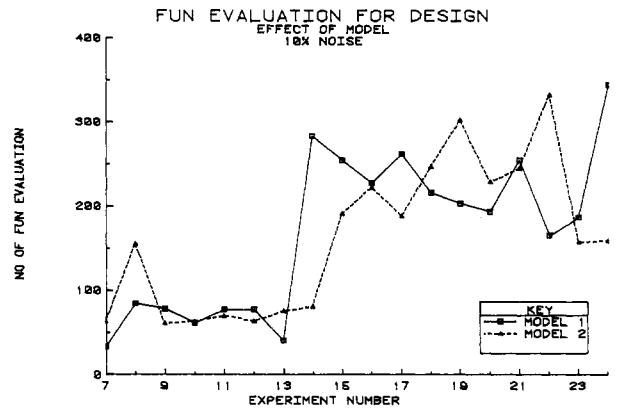

Figure 3. Number of function evaluations for optimal experimental design vs. experiment number (10% noise).

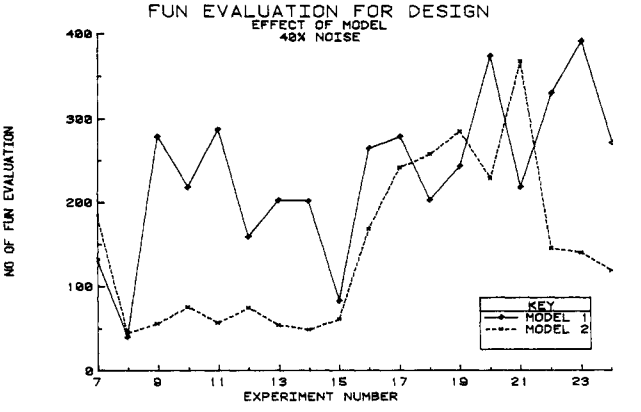

Figure 4. Number of function evaluations for optimal experimental design vs. experiment number (40% noise).

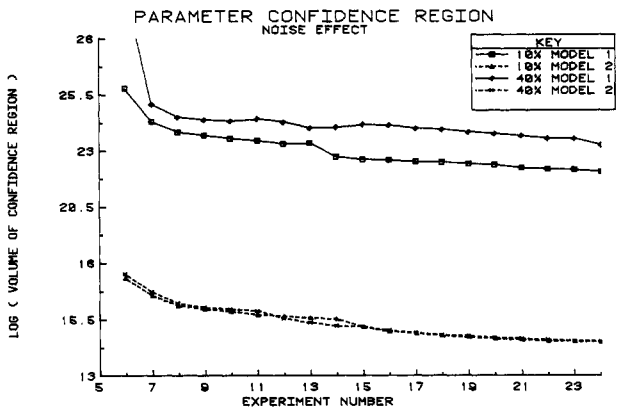

Figure 5. Volume of parameter confidence region vs. experiment number.

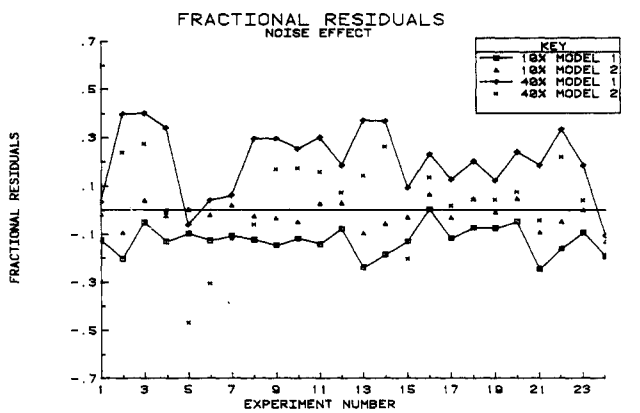

Figure 6. Fractional residuals vs. experiment number.

variables rapidly becomes flat. This flatness was also noted by Graham and Stevenson (1972). It is proposed that this phenomenon can easily be used as a stopping criterion for sequentially designed experiments by observing the number of function evaluations for the experimental design. It is evident from Figure 3 that as the surface becomes flat the number of function evaluations to design the independent variables increases sharply for the low noise case, for both models. Figure 4, however, shows that at higher noise the design surface for the non-RP model does not show such well-defined behavior, while the design surface of the RP model is quite immune to noise effects.

Table III compares the parameter values and their deviations from the true values, for 40% noise, at the 15th experiment, after which the surface becomes flat. It is evident that the values of E and α were estimated very accurately even at high noise by the RP model, while values of A_0 and β were reasonably good compared to the non-RP model. The deviations in A_0 and β are still significant because the correlation between θ and β in the RP model (eq 11) is relatively high (Table IV). However, the correlation between θ and ϕ in the RP model is reduced to the negligible value of 0.10 compared to correlation between A_0 and E, greater than 0.99, in the non-RP model.

The effects of noise and reparameterization on the size of the parameter confidence region (measured by $|\mathbf{D}^T\mathbf{D}|^{-1/2}$) are shown in Figure 5, which clearly demonstrates the negligible effect of noise on the confidence region of the RP model. The size of the confidence region for the parameters is a measure of the uncertainty of the estimates, and its shape and size depend upon the parameter values. In the RP model all four parameters are of comparable order of magnitude (see Table I), while in the non-RP model the values span four orders of magnitude. This

Table II. Simulated Experimental Conditions[a]

expt no.	temp, °C	$X_{C_2H_4}$	X_{H_6}
1	45.0	0.35	0.65
2	53.0	0.30	0.70
3	60.0	0.28	0.72
4	68.0	0.38	0.45
5	75.0	0.25	0.55
6	85.0	0.15	0.60

	temp, °C		$X_{C_2H_4}$		X_{H_6}		
expt no.	model 1	model 2	model 1	model 2	model 1	model 2	noise, %
7	90.00	90.00	0.10	0.10	0.40	0.40	10
	82.09	82.09	0.40	0.40	0.60	0.60	40
8	85.80	85.80	0.10	0.10	0.80	0.80	10
	90.00	90.00	0.40	0.40	0.40	0.40	40
9	67.43	67.43	0.10	0.10	0.80	0.80	10
	85.80	90.00	0.10	0.40	0.80	0.40	40
10	90.00	67.51	0.10	0.10	0.40	0.80	10
	80.76	74.67	0.21	0.40	0.79	0.40	40
11	67.81	90.00	0.10	0.10	0.80	0.40	10
	82.09	72.71	0.40	0.40	0.60	0.40	40
12	67.81	68.00	0.10	0.10	0.80	0.80	10
	80.82	90.00	0.20	0.10	0.80	0.66	40
13	90.00	90.00	0.10	0.10	0.40	0.40	10
	90.00	90.00	0.10	0.10	0.66	0.40	40
14	82.09	68.30	0.40	0.10	0.60	0.80	10
	80.82	90.00	0.20	0.10	0.80	0.40	40
15	80.82	90.00	0.20	0.40	0.80	0.42	10
	70.68	90.00	0.10	0.10	0.80	0.40	40
16	90.00	82.09	0.40	0.40	0.42	0.60	10
	80.82	85.80	0.20	0.10	0.80	0.80	40
17	80.82	80.82	0.20	0.20	0.80	0.80	10
	80.82	85.80	0.20	0.40	0.80	0.80	40
18	80.82	85.60	0.20	0.10	0.80	0.80	10
	82.47	82.03	0.40	0.40	0.59	0.60	40
19	90.00	82.10	0.40	0.40	0.42	0.60	10
	80.82	82.09	0.20	0.40	0.80	0.60	40
20	85.80	85.80	0.10	0.10	0.80	0.80	10
	63.69	85.80	0.20	0.10	0.80	0.80	40
21	82.09	85.80	0.40	0.10	0.60	0.80	10
	90.00	80.84	0.10	0.20	0.66	0.80	40
22	65.58	82.09	0.40	0.40	0.60	0.60	10
	63.62	65.65	0.20	0.20	0.80	0.80	40
23	65.62	66.23	0.40	0.40	0.60	0.60	10
	63.45	65.29	0.20	0.20	0.80	0.80	40
24	80.82	66.20	0.20	0.40	0.80	0.60	10
	80.82	65.19	0.20	0.20	0.80	0.80	40

[a] Nitrogen is used as diluent, total pressure 1 atm.

Table III. Parameter Estimates at the 15th Experiment (40% Noise)

	model 1		model 2	
param	param value	rel dev, %	param	rel dev, %
A_0	1.029×10^5	$+2.1 \times 10^3$	2.799×10^3	−39.5
E	1.334×10^4	+15.0	1.153×10^4	−0.6
α	0.522	+58.2	0.309	−6.4
β	1.870	+87.0	0.611	−38.9

point tends to emphasise that a model should always be a candidate for some type of reparameterization or transformation of parameters if the parameter values have a larger span than an order of magnitude.

Figure 6 shows the effect of noise on the fractional residual ((observed rate − predicted rate)/observed rate) for sequential experiments. It is apparent that the RP model is far superior to the non-RP model, with the RP residuals lying almost entirely within an evelope defined by the non-RP residuals. Also, the number of function evaluations in the parameter estimation is much smaller for the RP model compared to the non-RP model—for example, 110 and 553, respectively, for the seventh experiment at 10% noise.

Conclusions

It is seen from this example that the RP model leads to better parameter estimates in a sequentially designed

Table IV. Correlation Coefficients between Parameters (40% Noise)

	model 1				model 2			
	A_0	E_0	α	β	θ	ϕ	α	β
after preliminary experiments	1	0.9993	0.9770	0.9317	1	0.9699	0.9874	0.9574
		1	0.9709	0.9226		1	0.9700	0.9251
			1	0.9026			1	0.9035
				1				1
after 15th experiment	1	0.9973	0.5187	0.5191	1	−0.1055	0.5658	0.7278
		1	0.4603	0.4681		1	0.4113	0.4070
			1	0.6615			1	0.3630
				1				1

experimental program, even with strongly correlated parameters and high experimental noise levels. This model not only reduces the correlation among the parameters but reduces significantly the volume of the confidence region of the estimated parameters. Its use leads to more economical experimentation, with savings in computing time required, and the potential for equivalent parameter precision with fewer experiments. While the availability of a statistical technique less sensitive to noise should not be advocated as an excuse to permit poorly designed or performed experiments, it appears that the RP model will tolerate very noisy data and allow an experimental program to converge to meaningful results not otherwise obtainable. This is of significance in awkward industrial experimental situations.

Finally, with the RP model, a sudden increase in the number of function evaluations for the optimal design appears to be a useful criterion for terminating the sequential experimental program.

Nomenclature

A_0 = preexponential factor in Arrhenius expression, eq 1
$\mathbf{D}$ = $(n \times p)$ matrix of element $\partial f(\mathbf{X}_u,\mathbf{K})/\partial \mathbf{K}_j$
E = activation energy in the Arrhenius expression, eq 1
k = reaction rate constant
k^* = reparameterized Arrhenius preexponential factor, eq 3
$\mathbf{K}$ = vector of model parameters
m = number of operating variables
n = number of experiments
p = number of model parameters
$r_{C_2H_6}$ = rate of formation of ethane
R = ideal gas constant
T = absolute temperature
T^* = reference temperature
$T' = 1/T - 1/T^*$, eq 12
$\mathbf{V}$ = $(p \times p)$ covariance matrix for parameter estimates
$\mathbf{X}_u$ = vector of operating variable settings for experiment u
$X_{C_2H_4}$ = mole fraction of ethylene
X_{H_2} = mole fraction of hydrogen
y_u = measured reaction rate for experiment u

Greek Symbols

α = reaction rate order with respect to ethylene
β = reaction rate order with respect to hydrogen
ϵ = random error
θ = defined in eq 13
ϕ = defined in eq 14
σ^2 = variance of random error

Subscript

u = experiment number

Superscript

$\hat{}$ = least-square estimate

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Sequential Experimental Design for Precise Parameter Estimation. 2. Design Criteria

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Three different criteria which have been proposed for sequentially designed experiments to estimate parameters precisely in kinetic models have been compared. Criteria which seek to alter the shape of the joint confidence region of the parameter estimates or to reduce cross correlation effects were proved useful, but the minimum volume criterion emerges as the most generally satisfactory criterion for the conditions likely to arise in industrial experimentation.

Introduction

The problem of planning an experimental program to estimate parameters precisely in reaction rate models has received considerable attention in the past two decades. Some useful techniques have been developed for the estimation of rate constants in nonlinear models. Box et al. (1959, 1965) pioneered the investigation of a sequential experimental design criterion by which experimenters select their conditions to yield the most precise estimates of parameters. They achieved this by minimizing the volume of the joint confidence region of the parameter estimates.

Recently, two new design criteria have been reported in the literature. These criteria were developed with specific aims. Pritchard and Bacon (1978) chose to reduce the correlation among the parameter estimates. Hosten (1974) sought to make the joint confidence region of the estimates as spherical as possible. These authors compared their criteria with the design criterion of Box et al. and each

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