concentrations in the effluent gas. Also the fractions absorbed in the dichloromethane trap were unknown. However, the analyses suggested that only a small amount of the total material was desorbed as phenol or diphenyl ether. Presumably, most of the desorbed substance were cracked products.

CONCLUSIONS

The results that we have found show that drying in air at 393 K results in desorption of 38% of the initial weight of phenol adsorbed on carbon from aqueous solutions. Subsequent heating to 673 K caused an 11% loss in weight of the material remaining at 393 K. Water, carbon dioxide, and very small amounts of phenol and diphenyl ether were identified as some of the desorption products in this temperature range, but UV analysis indicated that other species were also being desorbed. Additional heating to 1,073 K resulted in a further 42% loss in the weight of material remaining at 393 K. Phenol, and particularly cracked products, were desorbed in this high-temperature range. Of the material remaining after drying at 393 K, there was a residue of 47% after heating to 1,073 K.

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NOTATION

$\dot{m}$ = rate of weight loss, kg/(s) (kg of virgin carbon)
q = mass adsorbed/(mass of virgin carbon); q_o = mass adsorbed initially
T = temperature, K

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Statistically Rigorous Parameter Estimation in Dynamic Modeling Using Approximate Empirical Models

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INTRODUCTION

In the last few centuries the tools of physics have been developed to the stage that sets of predictive equations, called models, for many natural phenomena can be constructed. These models usually take the form of differential and integral equations that must be solved numerically. Although numerical simulation and algorithm efficiency are presently common topics, the most important questions of modeling, namely adequacy and statistical reliability of the proposed dynamic models, have not received appropriate attention. It is precisely these aspects that must finalize the model building process.

The goal of modeling is to deduce the mathematical description of a physical process. Typically, this mathematical description takes the form of a mechanistic model. In such models we believe the governing equations are tentatively known but the values of physical constants, called parameters, must be determined. The basic philosophy of modeling has been developed by Box and coworkers (Box and Hunter, 1965; Box and Draper, 1965; Box et al., 1973; Box et al., 1978) who proposed general criteria for parameter estimation defined in terms of model responses. Particular attention in their works was given to model adequacy which they assessed through an analysis of the confidence regions for the parameters. Their ideas were discussed using a number of simple models which allow analytical solutions.

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TABLE 1. RESULTS OF THE INITIAL DESIGN

$$\begin{pmatrix} \ell n[CH_4]_{700} \\ \ell n[C_2H_4]_{700} \\ \ell n[C_2H_6]_{700} \\ \ell n[C_3H_6]_{700} \\ \ell n[H_2]_{700} \end{pmatrix} = \begin{pmatrix} -50.23 & 0.427 & 1.60 & -0.0563 & -0.0126 & 0.00602 \\ -39.31 & 0.830 & 0.857 & 0.0 & 0.0 & 0.0 \\ -34.05 & 0.675 & 1.05 & -0.119 & -0.0220 & 0.0163 \\ -34.53 & 0.929 & 0.408 & -0.0559 & 0.00953 & -0.0146 \\ -17.87 & 1.218 & 0.876 & -0.0505 & 0.0343 & -0.0251 \end{pmatrix} \times \begin{pmatrix} 1 \\ \ell nk_1 \\ \ell nk_2 \\ (\ell nk_1)^2 \\ (\ell nk_2)^2 \\ \ell nk_1 \ell nk_2 \end{pmatrix}$$

There are two major difficulties in applying Box and coworkers methods to complex dynamic models. The first is technical, in that many response calculations must be performed during the optimization procedure, which may place large demands on computer time. The second, perhaps more critical, difficulty is the large number of parameters to be determined which often leads to a negative number of degrees of freedom.

Because of these difficulties the approach normally taken by researchers is to numerically integrate the appropriate differential equations and compare the computed responses with experimental data. If the calculations agree with the data, the model is accepted as valid. If they do not agree, the parameters are revised and another integration is performed. This process is repeated until the model "fits" the data. Although suitable as a computer exercise, such a trial-and-error approach lacks statistical rigor and may lead to wrong conclusions (Frenklach, 1984).

To guide the selection of parameters and to adjust their values the modeler usually relies on sensitivity analysis (Frank, 1978; Frenklach, 1984) which provides a set of partial derivatives of model responses with respect to model parameters. However, sensitivity analysis by itself does not resolve the principle issue of model adequacy. First, the sensitivity information has a physical meaning only when the model itself is *adequate*, at least in the statistical sense. Second, most methods provide only "point" estimates of sensitivities, sensitivities which are evaluated at a given point in the parameter space. In general, sensitivities will change from one point to another. Third, one usually finds that individual sensitivities are correlated which complicates their interpretation. The method proposed in this paper incorporates parameter estimation, test for adequacy, and sensitivity analysis in a unified model building procedure.

METHOD

Parameter estimation is based on the functional relationships between responses and unknown parameters, specified analytically or numerically. We suggest to develop these relationships for a given dynamic model in an empirical manner via computer experimentation. In this approach a set of computer simulations are performed at preselected values of the parameters. Statistical analysis of the computational results provides the required functional relationship. Applying the techniques of experimental design increases the efficiency of this approach.

A concept of computer experiment was originally introduced by Box and Coutie in 1956. They proposed to employ computer experimentation for the problem of optimization, for which the global objective function was approximated by a second-order polynomial in the parameters. Following their ideas we suggest to employ computer experimentation to determine an empirical relationship for *individual* responses. Once these empirical models are developed and their statistical adequacy confirmed, they can replace the dynamic model in the further stages of model development.

The advantage of this approach is twofold. First, sensitivity information is now provided by directly differentiating the derived empirical relationships. In this manner sensitivities and their interrelationships are obtained for any point of parameter space within, of course, the region of adequacy of the empirical relationships. Second, parameter estimation and analysis of adequacy for the original dynamic model can be assessed by the well developed methods of Box and coworkers, for which the empirical relationships provide the required information on the responses.

The method has recently been demonstrated with an example drawn from the field of chemical kinetics (Miller and Frenklach, 1983). For the details of the example we refer the reader to the cited article; here we will limit the discussion to the main framework of the technique.

A reaction mechanism of 11 reactions and 11 species which describes the shock-tube decomposition of propane at approximately 1,100 K (Lifshitz and Frenklach, 1975) was considered. Two reaction rate constants were to be estimated based on the concentrations of five products at a reaction time of 700 μs by Lifshitz et al. (1973). The mathematical description of the system takes the form of a dynamic model, that is for each reaction species

$$\frac{dc_j}{dt} = \sum_i v_{ij} k_i \prod_\ell c_\ell \qquad ,j = 1,2,\ldots,11 \tag{1}$$

with the specified initial conditions. At a given time, t, the solution of Eq. 1 may be thought of as

$$c_{j,t} = f_{j,t}(\mathbf{k}) \tag{2}$$

where functions $f_{j,t}$ are defined numerically. In this example, these functions at $t = 700$ μs determine the relationships between the five responses, c_r ($r = 1,2,\ldots,5$), and the two parameters, k_1 and k_2,

$$c_r = f_{r,700}(k_1,k_2). \tag{3}$$

The essence of the method is to approximate the functions $f_{r,700}(k_1,k_2)$ by an empirical model, which can be determined through computer experimentation. In this example, we sought a polynomial form

$$\ell nc_r = a_{0r} + a_{1r}\ell nk_1 + a_{2r}\ell nk_2 + a_{11r}(\ell nk_1)^2 + a_{22r}(\ell nk_2)^2 + a_{12r}\ell nk_1\ell nk_2 + \ldots \tag{4}$$

by employing sequential factorial design of computer experiments. As there is no experimental error in the computations, it is easy to test the adequacy of the empirical model employing criteria discussed by Box and Draper (1982). This procedure actually specifies the ranges of parameter values for which the empirical model adequately replaces the dynamic model.

The results of the procedure are given in Table 1 in the form of a matrix equation. Required sensitivities can be obtained by directly differentiating the appropriate equation, for example,

$$S_1^4 \equiv \frac{\partial \ell n[C_3H_6]_{700}}{\partial \ell nk_1} = 0.929 - 0.1118\ \ell nk_1 - 0.0146\ \ell nk_2. \tag{5}$$

Sensitivities determined in this way are valid within the region of parameter space for which the empirical approximations are valid.

The same empirical expressions for the responses can be used for parameter estimation. In our case the general criteria for multiresponse parameter estimation degenerates to least squares, i.e. to the minimization of the objective function, $\phi(k_1,k_2)$ given by

$$\phi(k_1,k_2) = \sum_r (\ell nc_{r,\text{expt}} - \ell nc_{r,\text{calc}})^2. \tag{6}$$

Optimization found the minimum of the objective function at a point outside the original range of the factorial design. Therefore the entire procedure was repeated with another design centered at the previously found minimum, which concluded with satisfactory results.

Determination of a confidence region utilizing the empirical model becomes a trivial task. It is obtained by solving equation 6 together with

$$\phi(k_1,k_2) = \phi_{\min}\left\{1 + \frac{p}{n-p} F_{5\%}(p,n-p)\right\} \qquad (7)$$

and using the established relationships for $c_{r,\text{calc}}$. For this example, the analysis of confidence regions, detailed in Miller and Frenklach (1983), revealed certain features of the experimental data which were not detected originally.

NOTATION

a = coefficients of empirical Eqs. 4
c (or [ ]) = species concentration
$F_{5\%}(p,n-p)$ = upper 5% point of F distribution with p and $n-p$ degrees of freedom
f = numerically defined solution for Eq. 1
k = reaction rate constant
$\mathbf{k}$ = vector of reaction rate constants
n = number of observed responses
p = number of adjustable parameters, 2 in this example
S_i^r = logarithmic sensitivity of rth resposne to ith rate constant
t = reaction time

Greek Letters

υ_{ij} = generalized stoichiometric coefficient of jth species in ith reaction
ϕ = objective function
$\phi_{\min}$ = the minimum value of the objective function

Subscripts

i = reaction number
j = species number
r = response number
t = at time t

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Predicting the Holdup in Two-Phase Bubble Upflow and Downflow Using the Zuber and Findlay Drift-Flux Model

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INTRODUCTION

Relatively recent development of the deep shaft reactor (Collins and Elder, 1980; Cox et al., 1980; Kubota et al., 1978) and interest in similar devices of smaller bore (Clark and Flemmer, 1983) have demanded a better understanding of two-phase downflow in pipes. DSRs operate as mass transfer devices using vertical bubble flow. Knowledge of the gas void fraction present in the pipe is essential for the prediction of hydrostatic head, a factor influencing mass transfer rate. Upward two-phase flow has received much attention in the literature, but downflow a good deal less. Both upflow and

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