

SRC-TR-87-81

**CHEMICAL PROCESS SYSTEMS
LABORATORY**

Estimation of Reaction Kinetic Parameters
by Local On-Line Experimentation

by

O. A. Asbjornsen
P. S. Robinson

RESEARCH REPORT

CHEMICAL PROCESS SYSTEMS ENGINEERING LABORATORY

ESTIMATION OF REACTION KINETIC PARAMETERS BY LOCAL
ONLINE EXPERIMENTATION

O. A. Asbjornsen and P. S. Robinson

**A CONSTITUENT LABORATORY OF
THE SYSTEMS RESEARCH CENTER**

**THE UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND 20742**

ESTIMATION OF REACTION KINETIC PARAMETERS BY LOCAL ONLINE EXPERIMENTATION.

O. A. Asbjornsen and P. S. Robinson.

University of Houston-University Park
Department of Chemical Engineering
4800 Calhoun, Houston, TEXAS 77004

ABSTRACT

In the control of chemical reactors, it is important to know the kinetic parameters of the reaction with good precision. The traditional approach is to try to estimate them from laboratory experiments or from plant records, where variations due to control or to disturbances may occur. However, this may happen only sporadically in the plant history because the reactor is at steady state for long periods of time. It would be advantageous to experiment online, so that the estimation of the kinetic parameters could be made more accurately and independently of plant changes.

This paper presents such a method which may be applicable to most industrial reactors. A test reactor is installed in parallel to the main stream and a little side stream to this reactor is taken from the main reactor stream at any point. In the simplest possible case, the side stream is led to a batch reactor where the reaction kinetics may be followed very closely. From the batch results it is possible to infer the kinetic parameters and even the order and mechanisms of the reactions. Such parameters shown here are the parameters in the Arrhenius type rate expression, the order and the heat of the reaction.

INTRODUCTION

In many examples where chemical reactors are controlled by a predictive feed forward algorithm [1,2,3] advantages may be taken of a front end test reactor in a little side stream from which the kinetic parameters may be estimated. There are several modes in which such a test reactor may be operated, in a steady state flow through mode with varying holding time, in a batch mode with a given sequence of charging and discharging and finally in a dynamic mode where process conditions like temperature and concentrations are changed as functions of time.

A practical case of online kinetic parameter estimation was implemented by the Borregaard Company [4] about thirteen years ago on a pulp bleaching plant. The kinetic model was used to predict the required consumption of bleaching chemicals down the line of the complete bleaching process.

The motivation for this was that the kinetic parameters in the bleaching reaction were found to be functions of the nature and concentration of the lignin in the pulp, and these properties were changing with the quality and type of the pulp.

A similar idea was attempted by the DeNoFa Company and published by Hertzberg and Asbjornsen [5,6] about the same time for the estimation of kinetic parameters in the hydrogenation reactions for unsaturated fatty oils. The purpose of this online batch reactor experimentation was to get the kinetic parameters for the prediction of the batch time, catalyst concentration and hydrogen pressure to hit the target specification for

the large scale batchwise hydrogenation reaction for the fatty oils.

There are several problems related to the general application of kinetic parameter estimation which will be touched upon in this paper. Even the simplest single reaction has at least two possible observations, the temperature and the concentration of a reactant or a product, but the concentration is usually much more difficult to measure. The parameters in a single first order reaction with Arrhenius kinetics [7] are known to be very strongly correlated [8], their regression model strongly nonlinear and their estimated values sometimes ambiguous. Some of these aspects are examined in this paper without going into the basic details or theoretical discussions.

In a kinetic experiment, there are several sources of errors and uncertainties. One obvious source is found in the process itself. If the experiment is assumed to be carried out in a complete mixing tank, the mixing may be incomplete in reality and introduce substantial disturbances on the kinetics. Another source of disturbance is the measurement of the temperature and concentration themselves which may have sensor noise or sampling noise.

For a given kinetic expression it is important to figure out how these disturbances and noise terms are going to affect the parameter estimates. One way of doing just that is to carry out simulation studies before the test reactor is actually implemented on the plant site. In such a numerical experiment, it is possible to compare the estimate with the correct answers which are known from the model. In the real life, the problem is exactly the other way around. However, a simulation study is indeed powerful in disclosing if a specific method of experimentation or parameter estimation is valuable or not.

A PARALLEL TEST REACTOR.

A small test reactor is mounted close to the main stream and a little side stream passes through the test reactor as shown schematically in figure 1. The value of this side stream (q) makes it possible to adjust the holding time (V/q) of the test reactor within a wide range. It may even be shut off for regular periods of time, allowing for the test reactor to operate in batch mode. The batch mode is likely to be the best mode of operation from a parameter estimation point of view, as this corresponds to a 0-1 square wave of the flow with a complete cleaning of the reactor between the batches.

When the reactor is operated in a batch mode the problem of determining the flowrate disappears and the volume of the reactor becomes immaterial as long as there are no exchange with the environment. This is a logical assumption one would try to meet in the design of the test reactor. In figure 1 is shown how the reactor is instrumented with a temperature and a concentration measurement. If there is an appreciable heat of reaction it would indeed be desirable to follow the reaction by the temperature alone, because this is a much easier and more

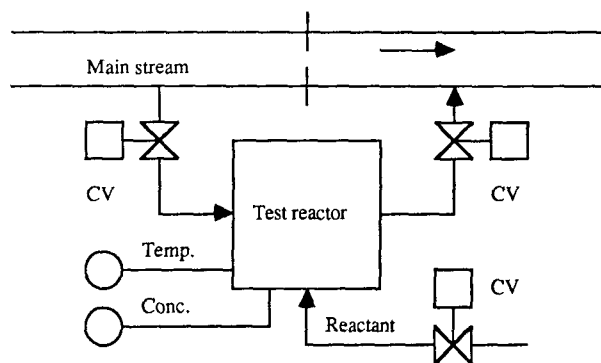


Fig. 1. A parallel test reactor for analytical purposes.

accurate measurement. The evaluation of this point is one of the major tasks in the preliminary simulation study of the measuring principle.

The batch reactor is also very easy to model for analytical purposes, but some basic assumptions have to be made. If use is made of the temperature information the reactor should preferably operate in adiabatic mode and this is assumed. Furthermore it is assumed that the reactor has a thorough and complete mixing.

A BATCH REACTOR MODEL

The batch reactor is assumed to be the basis for the estimation of the kinetic parameters, and only one single reaction is considered. This is by far the most common situation in industrial practice. The modeling task is then very simple, as the material balance of the reactant and the energy balance of the heat are sufficient equations leading to:

$$dc/dt = r(c,T) \quad (1)$$

and:

$$dT/dt = \Delta T(dc/dt) \quad (2)$$

The most general expression for a single reaction kinetic would be of the form:

$$r(c,T) = kc^a \exp(-E/RT) \quad (3)$$

There are basically four parameters in this kinetic model to be estimated for later use in feed forward control, the frequency factor k , the order of the reaction a , the normalized activation energy E/R and the adiabatic temperature rise per unit reactant ΔT . To simplify, the parameters and the state variables are normalized against their initial values in the batch reactor. Those values may be obtained *a priori* with a fairly high precision when the reactor is charged. The parameters and the state variables are defined:

$$\mathbf{p}^T = [p_1, p_2, p_3, p_4] = [kc_0^{a-1}, a, -E/(RT_0), \Delta Tc_0/T_0] \quad (4)$$

and:

$$\mathbf{x}^T = [x_1, x_2] = [c/c_0, T/T_0] \quad (5)$$

which give a normalized set of the model differential equations:

$$dx_1/dt = p_1 x_1^a \exp(p_3/x_2) \quad (6)$$

and:

$$dx_2/dt = p_4 dx_1/dt \quad (7)$$

At each observation point during the course of the batch reaction four variables may be established, the rate of change of the state variables and the state variables themselves. The rate of change is approximated by:

$$dx/dt = (x(k) - x(k-m))/(m\Delta t) \quad (8)$$

where Δt is the sampling time of the data acquisition system.

The reason why a certain number of samples m are picked for the calculation of the derivative is that this gives a balance between the required accuracy of the approximation of the derivatives and the effect of attenuation of the noise in the measured variable for their calculation.

MODELING PROCESS DISTURBANCES AND MEASUREMENT NOISE

In a realistic industrial application the world is different from the world of models and simulations. The first and major difference is that a realistic picture of noise and disturbances is not known or experienced by the model developer. However, some of these shortcomings may be helped by simulation. Reasonable assumptions may again be set up for this situation, and two conditions are considered specifically here. Those are the conditions related to the process disturbances and the conditions related to the measurement noise.

Process noise in an adiabatic batch reactor is really related to the turbulent mixing in the reactor giving rise to fluctuations in the reaction rate and in the process state variables. In order to understand the mechanism of this noise, one may look at the physical background of the process model.

Equation (1) and (2) are really volume averages which should be written:

$$V^{-1}d(\int cdV)/dt = V^{-1}\int r(c,T)dV \quad (9)$$

and:

$$V^{-1}d(\int TdV)/dt = -\Delta T V^{-1}d(\int cdV)/dt \quad (10)$$

If the assumption of complete mixing is not met in the physical test reactor, the consequence will be time variations in the volume averages. Since the root of the variations is found in the turbulent flow pattern and in the reaction itself, a simple model for the process disturbance phenomena would be to assume the fluctuations proportional to the reaction rate. Hence, all the turbulent effects on concentration may be incorporated in a stochastic parameter that affects the reaction rate by a proportionality factor:

$$dx_1/dt = (1 + e_1)p_1 x_1^a \exp(p_3/x_2) \quad (11)$$

Similarly, all the turbulent effects on the temperature may be incorporated by a another stochastic proportionality factor that affects the heat of reaction:

$$dx_2/dt = (1 + e_2) dx_1/dt \quad (12)$$

Naturally these factors are most likely correlated because their root is the same family, and that will make the resulting fluctuations in the concentration and temperature correlated also. Nevertheless, the disturbance model suggested above is rational and extremely simple and is adopted for the investigation of the effects of this kind of disturbances on the kinetic parameter estimation.

There is also noise on the measurements of concentration

and temperature, partly caused by the sensors themselves but to a greater extent by the fluctuations at the location of the sensors or in the sampling device. For simplicity, these fluctuations are also assumed to follow a proportionality relation between the sensor output y and the state x :

$$y_1 = (1 + e_3)x_1; \quad y_2 = (1 + e_4)x_2 \quad (13)$$

This disturbance and noise modeling also requires an assumption about the statistics of the stochastic variables. Again for simplicity in the present paper, the disturbance and noise phenomena are assumed to be white noise with zero mean and an amplitude probability density distribution described by a cosine distribution [9]:

$$dP/dx = 1 + \cos(2\pi x), \quad -1/2 < x < 1/2 \quad (14)$$

This is realized by a rectangular random number generator and a quantile function transformation of $P(x)$ in eqn (14).

PARAMETER ESTIMATION FROM THE BATCH EXPERIMENTS

The model considered is highly nonlinear and known to pose difficulties for parameter estimation. It is very tempting to transform the model equation to a logarithmic form, and this is obviously adequate for a noise free system. Therefore, four new variables are defined:

$$z_1(k) = \ln(-(y_1(k) - y_1(k-m))/(m\Delta t)) \quad (15)$$

$$z_2(k) = \ln((y_2(k) - y_2(k-m))/(m\Delta t))$$

$$u_1(k) = \ln(y_1(k)); \quad u_2(k) = 1/y_2(k) \quad (16)$$

and the noise free model equations may be written:

$$z_1(k) = \ln(p_1) + p_2 u_1(k) - p_3 u_2(k) \quad (17)$$

and:

$$z_2(k) = \ln(p_4) + z_1(k) \quad (18)$$

The parameter estimation minimizing the errors introduced by the approximation in eqn (8) is a straight forward linear regression as described in any textbook [10].

There are indeed some important comments that should be made at this stage. The logarithmic transformation is only allowed for monotonous change in temperature or decay of reactant concentration. This is the consequence of the assumptions suggested for the model, and if they are violated the model and the assumptions are incorrect.

According to the model the reaction is supposed to move in one direction and hence both k and c must be positive. A negative derivative or rate of change in the concentration is unacceptable. Such an observation is taken as an outlier violating the model and discarded. Should this ever happen frequently then the whole basis of the estimation procedure outlined here collapses. The inference principle assumes small errors in the model and in the measurement. If this assumption is not met then the transformation procedure and the test reactor are inadequate.

For the temperature the sign of the derivative follows the sign of the parameter p_4 but it has to keep the same sign during the complete course of the batch reaction. This is another consequence of the model formulation which takes it for granted

that there are only monotonous changes in temperature and concentration.

Therefore a special precaution is taken for the running calculation of the derivatives and the selection of the sample distance m . The introduction of m is equivalent to taking a mean value of the derivative over a period of time extended over several samples and this will contribute to avoiding sporadic outliers in the derivative caused by measurement noise. It should be noted that the process disturbances will never contribute to a negative rate of change. The rate may fluctuate but never become negative.

Parameter estimation in an error free simulated environment

It may seem trivial to carry out another demonstration of the comparison between *a priori* specified parameters and estimated ones in the world of simulated data. However, this is usually required in the practical applications because one would like this test to be performed on the algorithm to evaluate the goodness of the numerical calculations and the soundness of the various assumptions they are based on, for example given by eqn (8) above.

The batch reactor is simulated by a straight forward numerical integration based on a fourth order Runge-Kutta method [11] given the initial conditions of $x_0^T = [1,1]$ and the parameters $p^T = [2, 1.67, -3, -2]$. For a given set of sampling times, the integration is performed between the samples and the results at the sampling points are presented as the observed material.

The results are presented in Table 1, and it is seen that the parameter estimation is pretty insensitive to the sampling time below 0.05. Above that the adequacy of the derivative approximation is somewhat in doubt as the correspondance between estimated and true values of the parameters starts to deteriorate. At this point one is therefore in a fairly good position to recommend sampling times for the test reactor and the estimation method seems reliable if the process disturbances and the measurement noise can be kept under control.

| Sampling time | Estimated parameter values | | | |
|---------------|----------------------------|-------|--------|--------|
| | p_1 | p_2 | $-p_3$ | $-p_4$ |
| 0.01 | 2.010 | 1.670 | 3.008 | 2.000 |
| 0.03 | 2.029 | 1.669 | 3.023 | 2.000 |
| 0.1 | 2.096 | 1.668 | 3.074 | 2.000 |
| 0.3 | 2.288 | 1.660 | 3.220 | 2.000 |

Tab. 1. Parameter estimation in a noise free environment.

It is seen that the deterioration of the estimation algorithm with increasing sampling time is entirely due to the nonlinear nature of the model. For the parameter p_4 which enters a linear relationship between the temperature and concentration the sampling time has no observable effect. The effect on the reaction order is also fairly small. The activation energy and the frequency factor are known to be very strongly coupled, and what one sees in table 1 is exactly this effect. A small increase in the activation energy parameter reduces the exponential term and this is counteracted by an increase in the frequency factor to give the same response.

Parameter estimation in a noisy environment

If the disturbances and noise terms are relatively small the logarithmic transformation of the stochastic factors may be approximated by:

$$\ln(1 + e) = e \quad (19)$$

This is indeed logical, because the test reactor would be very badly designed if the error and noise terms were of any appreciable magnitude. The model equations may then be written:

$$e_1(k) = \ln(p_1) + p_2 u_1(k) + p_3 u_2(k) - z_1(k) \quad (20)$$

and:

$$e_2(k) = p_4 + z_1(k) - z_2(k) \quad (21)$$

The standard least square may be applied if the two noise terms are uncorrelated. If this is not the case, one should rather apply the maximum likelihood criterion and minimize the determinant of the covariance matrix of the residuals [12]:

$$F = E\{e_1^2\}E\{e_2^2\} - E\{e_1 e_2\}^2 \quad (22)$$

However, the way the regression equations are formulated, it becomes evident that the partial derivatives of e_2 with respect to any of the three first parameters and the derivative e_1 with respect to the last parameter are all zero, and the maximum likelihood for the parameter estimation coincides with the least square of the first model equation, eqn (20). Hence the parameter estimation in the noisy environment is identical to what was shown for the ideal noise free environment. In table 2 are shown some results of the parameter estimation for various levels of process disturbances and noise. The results are quite satisfactory for any realistic level of process disturbance and noise, and the test reactor may be used as an analytical instrument for kinetic parameter estimation, even with a very simplified and fast estimation routine.

| Process disturbances | | Measurement noise | | Parameter estimates | | | |
|----------------------|--------|-------------------|--------|---------------------|-------|--------|--------|
| Conc. | Temp. | Conc. | Temp. | p_1 | p_2 | $-p_3$ | $-p_4$ |
| .00001 | .00007 | | | 2.080 | 1.669 | 3.062 | 2.000 |
| .00001 | .00007 | .00003 | .00022 | 2.085 | 1.670 | 3.065 | 1.999 |
| .00005 | .00034 | | | 2.085 | 1.670 | 3.065 | 2.000 |
| .00005 | .00034 | .00012 | .00111 | 2.113 | 1.675 | 3.085 | 1.989 |
| .00027 | .00137 | | | 2.110 | 1.677 | 3.080 | 2.001 |
| .00027 | .00137 | .00062 | .00443 | 2.261 | 1.687 | 3.217 | 1.938 |
| .00136 | .00687 | | | 2.243 | 1.709 | 3.157 | 2.003 |
| .00136 | .00687 | .00310 | .02210 | 2.697 | 1.637 | 3.644 | 2.105 |

Tab. 2. Parameter estimation for a noisy test reactor.

In this table the number of samples used for the estimation of the time derivative is four everywhere except for the last case which is very noisy. The estimation of the derivative is here based on twenty samples. This corresponds to a time span of 0.4. The noise and disturbance levels are indicated as standard deviation in the normalized variables over the time of batch experimentation which is 6. The systematic bias errors in the parameter estimates are solely explained by the nonlinear nature of the model, as the terms e_1 and e_2 are stochastically independent.

Table 2 reconfirms the observation of the tight coupling between the activation energy and the frequency factor as those are the parameters strongest affected by the process disturbances and the measurement noise. It also becomes evident what is intuitively obvious, that the measurement noise is more important than the process disturbances which are attenuated through the lowpass characteristic of the test reactor.

The time needed for the analysis and estimation is determined by the time it takes to run a batch reaction experiment which again is determined by the rate of the reaction itself. But this is indeed the major variable which determines the speed at which the process would need analytical information of the reaction kinetics for the feed forward control.

PARAMETER ESTIMATION IN THE ABSENCE OF A CONCENTRATION MEASUREMENT

It would be very attractive to avoid the concentration measurement, because the general solution to that problem is much more complicated than to the temperature measurement. One is therefore tempted to develop a single observation model for kinetic parameter estimation and then use the temperature as the prime variable. One of the conditions for this to be possible is of course that the reaction has an appreciable heat of reaction and that the reactor wall heat capacity may be regarded as an extension of the fluid heat capacity. This means that any temperature difference between the reactor walls and its contents should be negligible and that the reactor should have practically perfect insulation.

Provided this is the case, one may calculate the concentration as a linear function of the initial conditions and the measured temperature. The initial conditions are given by the *a priori* charging of the reactor and are usually given with fairly high precision. The sensitivity between the temperature and concentration is given by the adiabatic temperature rise for the reactor and its contents expressed by the previous parameter p_4 :

$$y_1(k) = p_4^{-1}(y_2(k) - 1) + 1 \quad (23)$$

The model equation for the regression is now reduced to one single equation with slightly modified parameters, and may be written:

$$z_2(k) = p_1' + p_2 \ln(p_4' - y_2(k)) + p_3 u_2(k) \quad (24)$$

This equation turns out to involve two of the parameters in a somewhat complicated nonlinear fashion. As shown by Asbjornsen and Hertzberg [13], a regression problem of this nature is partitioned into a linear and a nonlinear subset. The nonlinear subset contains only two variables, and the parameter estimation is easily solved by a two-dimensional Newton iteration algorithm [13]:

$$p_1 = A^{-1} f_1(p_2) \quad (25)$$

and:

$$\Delta p_2 = -[(df_2/dp_1)A^{-1}(df_1/dp_2) + df_2/dp_2]^{-1} f_2 \quad (26)$$

where the partitioned parameter vector is:

$$p_1^T = [p_1', p_3], \quad p_2^T = [p_2, p_4']; \quad (27)$$

$$p_1' = \ln(p_1), \quad p_4' = p_4 + 1$$

and the functions f_1 , f_2 , $\partial f_1/\partial p_2$, $\partial f_2/\partial p_1$ and $\partial f_2/\partial p_2$ are:

$$f_{11} = \Sigma z_2(k) - p_2 \Sigma \ln(p_4' - y_2(k)); \quad (28)$$

$$f_{12} = \Sigma u_2(k) z_2(k) - p_2 \Sigma u_2(k) \ln(p_4' - y_2(k)) \quad (29)$$

$$f_{21} = p_1 \Sigma \ln(p_4' - y_2(k)) + p_3 \Sigma u_2(k) \ln(p_4' - y_2(k)) + p_2 \Sigma [\ln(p_4' - y_2(k))]^2 - \Sigma z_2(k) \ln(p_4' - y_2(k)) \quad (30)$$

$$f_{22} = p_2 [p_1 \Sigma (p_4' - y_2(k))^{-1} + p_3 \Sigma u_2(k) (p_4' - y_2(k))^{-1} + p_2 \Sigma \ln(p_4' - y_2(k)) (p_4' - y_2(k))^{-1} - \Sigma z_2(k) (p_4' - y_2(k))^{-1}] \quad (31)$$

$$\partial f_{1,11}/\partial p_2 = \Sigma \ln(p_4' - y_2(k)) \quad (32)$$

$$\partial f_{1,12}/\partial p_4' = p_2 \Sigma 1 / (p_4' - y_2(k)) \quad (33)$$

$$\partial f_{1,21}/\partial p_2 = \Sigma u_2(k) \ln(p_4' - y_2(k)) \quad (34)$$

$$\partial f_{1,22}/\partial p_4' = \Sigma u_2(k) / (p_4' - y_2(k)) \quad (35)$$

$$\partial f_{2,11}/\partial p_1' = \Sigma \ln(p_4' - y_2(k)) = \partial f_{1,11}/\partial p_2 \quad (36)$$

$$\partial f_{2,12}/\partial p_3 = \Sigma u_2(k) \ln(p_4' - y_2(k)) = \partial f_{1,21}/\partial p_2 \quad (37)$$

$$\partial f_{2,21}/\partial p_1' = p_2 \Sigma 1 / (p_4' - y_2(k)) = \partial f_{1,12}/\partial p_4' \quad (38)$$

$$\partial f_{2,22}/\partial p_3 = \Sigma u_2(k) / (p_4' - y_2(k)) = \partial f_{1,22}/\partial p_4' \quad (39)$$

$$\partial f_{2,11}/\partial p_2 = \Sigma (\ln(p_4' - y_2(k)))^2 \quad (40)$$

$$\partial f_{2,12}/\partial p_4' = p_1' \Sigma (p_4' - y_2(k))^{-1} - p_3 \Sigma u_2(k) / (p_4' - y_2(k))^{-1} + 2p_2 \Sigma \ln(p_4' - y_2(k)) / (p_4' - y_2(k)) - \Sigma z_2(k) / (p_4' - y_2(k))^{-1} \quad (41)$$

$$\partial f_{2,21}/\partial p_2 = \partial f_{2,12}/\partial p_4' \quad (42)$$

$$\partial f_{2,22}/\partial p_4' = -p_2 [p_1' \Sigma (p_4' - y_2(k))^{-2} + p_3 \Sigma u_2(k) (p_4' - y_2(k))^{-2} + p_2 \Sigma (1 - \ln(p_4' - y_2(k))) (p_4' - y_2(k))^{-2} - \Sigma z_2(k) (p_4' - y_2(k))^{-2}] \quad (43)$$

The matrix A is independent of the parameters and given by the elements:

$$a_{11} = \Sigma 1; a_{12} = a_{21} = \Sigma u_2(k); a_{22} = \Sigma u_2(k)^2 \quad (44)$$

Under the same conditions as the previous parameter estimations are the results of this particular case of a missing observation in the concentration summarized in table 3.

As it is seen from this table, the estimation of the kinetic parameters has not at all deteriorated due to the lack of observation of the concentration. On the contrary, the range of apparently useful estimation has been extended and the largest systematic error due to the nonlinearity has been shifted from the activation energy and the frequency factor to the order of the reaction.

The time range for the estimation of the temperature derivative is four samples except for the last where the estimation algorithm collapses. The noise is now so large that it took 40 samples, or a time span of 0.4, to get a reasonable estimate of the time derivative of the temperature. The results in the last line of table 3 are not reliable.

| Process disturbances | Measurement noise | | Parameter estimates | | | | |
|----------------------|-------------------|--------|---------------------|----------------|-----------------|-----------------|-------|
| | Conc. | Temp. | p ₁ | p ₂ | -p ₃ | -p ₄ | |
| .00001 | .00007 | | 2.027 | 1.619 | 3.027 | 1.979 | |
| .00001 | .00007 | .00003 | .00022 | 2.018 | 1.599 | 3.013 | 1.969 |
| .00005 | .00034 | | | 2.020 | 1.613 | 3.018 | 1.977 |
| .00005 | .00034 | .00012 | .00111 | 1.990 | 1.506 | 2.972 | 1.915 |
| .00027 | .00137 | | | 1.982 | 1.582 | 2.990 | 1.964 |
| .00027 | .00137 | .00062 | .00443 | 1.924 | 1.302 | 2.911 | 1.813 |
| .00136 | .00687 | | | 1.805 | 1.439 | 2.855 | 1.904 |
| .00136 | .00687 | .00310 | .02210 | 3.052 | 1.584 | 3.686 | 1.936 |

Tab. 3. Parameter estimation where the concentration is not observed.

As it is seen from this table, the estimation of the kinetic parameters has not at all deteriorated due to the lack of observation of the concentration. On the contrary, the range of apparently useful estimation has been extended and the largest systematic error due to the nonlinearity has been shifted from the activation energy and the frequency factor to the order of the reaction.

The time range for the estimation of the temperature derivative is four samples except for the last where the estimation algorithm collapses. The noise is now so large that it took 40 samples, or a time span of 0.4, to get a reasonable estimate of the time derivative of the temperature. The results in the last line of table 3 are not reliable.

CONCLUSION

A general concept of an online batch reactor for the estimation of the kinetic parameters in a process stream has been suggested. Fairly successful applications of this simple analytical instrument rely heavily on the design of the reactor and the adequacy of the model. If the suggested principle is tried out in industrial practice one should take the following precautions.

The mixing disturbances and noise in the batch reactor itself should be minimal. The design of the feed to the reactor and the mixing device should be given careful consideration. However, the mixing noise does not seem to be as important as the measurement noise.

The measurement noise is shown to be critical for the

inference of the reaction kinetic parameters. This is basically due to the nonlinear characteristics of the temperature sensitive rate constant. The well known interaction between the frequency factor and the activation energy is reconfirmed in this numerical experiment as well. Measurement noise should be kept to a lowest practical minimum, and this includes sensor noise, turbulent noise at the sensor location and eventual sampling noise by varying representativity of eventual samples.

For a single reaction with an appreciable heat of the reaction, it is shown that a simple temperature measurement for the inference of kinetic parameters is just as good as a principle where measurements of both temperature and concentration are involved. This is a result of such a great practical significance for industrial use that the principle should be given a thorough and careful investigation, both from a statistical side and from an experimental side.

The data processing involved in the inference of the reaction kinetic parameters avoids any nonlinear programming for optimization but solves the unconstrained parameter optimization as a standard set of nonlinear equations. The total set of optimality condition is shown to be partitioned into a linear and a nonlinear set. The algorithm is so simple that it is very well implemented on a small Personal Computer. The test version for this paper was run on an HP 9816 and programmed in HP BASIC.

SYMBOLS

| | | | |
|------------|-----------------------------|------|-------------------|
| A | constant matrix | a | exponent |
| a | matrix coefficients | c | concentration |
| ΔT | adiabatic temperature rise | e | error |
| E{ } | expectation operator | E/R | activation energy |
| F | determinant criterion | f, f | general functions |
| k | frequency factor | k | running index |
| m | number of samples | p,p | parameters |
| P | probability | r | reaction rate |
| T | temperature | t | time |
| u, u | regression variables | V | volume |
| x,x | normalized state variable | y, y | sensor output |
| z, z | logarithm of the derivative | | |

REFERENCES

- Vakil, H. B., M. L. Michelsen and A. S. Foss (1973): "Fixed Bed Reactor Control with State Estimation.", *AIChE JI.* **12**, 328-335.
- Gran, H., H. Grande and S. Lange (1976): "Optimal Control of Vinyl Chloride Polymerisation Reactors." *4th European Symp. on React. Engg.*, Heidelberg.
- Stephanopoulos, G. (1984): *Chemical Process Control - An Introduction to Theory and Practice.*, Prentice-Hall Inc., Englewood Cliffs, N. J.
- Kjerheim, G. (1973): *Personal Communication*, Borregaard Co., Fredrikstad, Norway.
- Hertzberg, T. and O. A. Asbjornsen (1972): "Hydrogenation of Fatty Oils - Mathematical Models Derived from Pilot Plant Experiments.", *Chisa Conf. Proc.*, Prague.
- Hertzberg, T. and O. A. Asbjornsen (1977): "Parameter Estimation in Nonlinear Differential Equations.", *Computer Applications in the Analysis of Chemical Data and Plants*, Science Press, Princeton, 155-165.
- Levenspiel, O. (1964): *Chemical Reaction Engineering.* John Wiley, New York.
- Hertzberg, T. (1972): "Test and Examples on the use of the Model Fitting System MODTLP.", *Norges tekniske hogskole*, Institutt for kjemiteknikk, Trondheim, Norway. (In Norwegian).
- Asbjornsen, O. A. (1982): "Modeling and Simulation for Computer-Aided Design and Operation of Chemical Plants.", *Lecture Notes, Danmarks tekniske Hojskole*, Institutet for Kemiteknik, Denmark.
- Draper, N. R. and H. Smith (1966): *Applied Regression Analysis.*, John Wiley, New York.
- Luyben, W. L. (1973): *Process Modeling, Simulation and Control for Chemical Engineers.*, McGraw-Hill Book Co. New York.
- Goodwin, G. C. and R. L. Payne (1979): *Dynamic Identification - Experiment Design and Data Analysis.* Academic Press, New York.
- Asbjornsen, O. A. and T. Hertzberg (1974): "Constrained Regression in Chemical Engineering Practice.", *Chem. Engg. Sci.* **29**, 679-687.