A Computational Method of Estimating Parameters in Rate Equations of Fat Hydrogenation

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ABSTRACT AND SUMMARY

A computational method for fitting a simplified mathematical model of fat hydrogenation reactions to experimental kinetic data is given. The parameters of the mathematical model were estimated by a nonlinear least-squares regression technique, and the minimum search method included was tested on a special function with a narrowed curved valley.

INTRODUCTION

Electronic computer methods, analog as well as digital ones, are often used in the study of problems in lipid chemistry (1). Different computer methods have been of great value in illustrating selectivity properties of fat hydrogenation (2) or in calculating the parameters in the rate equations of fat hydrogenations (3-5).

Regarding the kinetics of fat hydrogenation, only very simple models were studied at the beginning of the computer era. During this period of time, a set of relative rate constants were calculated for every temperature and hydrogen pressure, and the rate constants were valid only under very specific mass transfer conditions with respect to the hydrogen transport from the gas phase to the catalyst. The hydrogenation was generally assumed to be of zero order with respect to the hydrogen concentration. The influence of the hydrogen concentration was instead included in the apparent rate constant. Reactor control, optimization and scale-up studies, all require mathematical models of more general validity. These models are subsequently more complicated, and more advanced computational methods are necessary to calculate the parameter values in these models.

The rapid development in computer technique has now made it possible to solve very complex problems in parameter estimation, and a great number of general methods have been published for the calculation in reaction modeling (6). Most of these methods are quite general and must first be modified in order to be applicable to a specific problem. In fat hydrogenation kinetics, the reaction model consists of a set of nonlinear differential equations. The equations are coupled, since the reaction network consists of both parallel and consecutive reactions. One characteristic of the reaction model is the fact that one component (hydrogen) is supplied continuously to the reaction mixture and the concentration of this component is independent of the progress of reaction. Under ideal reaction conditions, this concentration is, moreover, constant, which simplifies the calculation procedure. In most hydrogenations, the kinetic study is complicated by the fact that the hydrogen concentration is dependent on the mass transfer conditions near the phase contacts. The hydrogen concentrations in the reaction zone will thus be lower than the solubility hydrogen concentration, and, in addition, the hydrogen concentration increases during the hydrogenation owing to the slow decrease of reaction rate during the process.

In the present article, a computational method especially adopted for fat hydrogenation modeling will be given. The method was tested for a kinetic model of rapeseed oil hydrogenation.

GENERAL DESCRIPTION OF THE COMPUTATIONAL PROCEDURE

The unknown parameters to be determined in a power type rate equation (see eq. II below) are the pre-exponential factor of the rate constant, the Arrhenius activation energy, and the reaction orders. Since the rate equations of fat hydrogenations are nonlinear, there is no direct method for calculating the parameter values. Instead the rate equations have to be integrated numerically with different sets of parameter values until the predicted and experimental concentrations of fatty acids agree as well as possible. As mentioned above, the concentration of hydrogen must be calculated parallel to this integration from the mass transfer equation. The rate of hydrogen mass transfer is calculated from the rate of reactions and, subsequently, is dependent on the fatty acid concentration obtained by the integration. If the number of simultaneous reactions is very great, as in rapeseed oil hydrogenation, it is preferable to calculate the hydrogen mass transfer rate separately from the rate of iodine value decrease, since this rate is related to the hydrogen reaction rate in a very simple way. The iodine values are easily calculated from the fatty acid composition.

The concentrations of fatty acids found by integration of the rate equations are compared with those experimentally found. The next set of parameter values needed to obtain better agreement between predicted and experimental concentrations are found with a special search technique described below. The final set of parameter values were chosen so that the sum of the squared differences between predicted and experimental concentrations was minimized, which means that the best fit was performed according to the least-squares regression criterion. Owing to the fact that the experimental concentrations of the various fatty acids vary considerably, the squared differences in the sum must be multiplied with different weights. To decrease parameter interaction, as for example between the pre-exponential factor and the activation energy, a re-parameterization was necessary.

A MATHEMATICAL DESCRIPTION OF THE COMPUTATIONAL PROCEDURE

In vegetable oils the fatty acids with eighteen carbon atoms, called C-18 acids in the present article, are most often the dominating fatty acids in the glycerides. When other fatty acids are present in excess, as in rapeseed oil, these acids will of course interfere with the hydrogenation of C-18 acids owing to the competition on the catalytic surface. Despite this competition, it is possible to describe the rate of hydrogenation with simple power type equations suitable for design purposes (7). When applied to hydrogenation of C-18 acids in rapeseed oil, this power type equation needs only include the weight fraction of the C-18 acid of interest and the hydrogen concentration. The parameters of this equation can subsequently be determined independently of parameters of the rate equations for the simultaneous hydrogenation of C-22 and C-20 acids in the rapeseed oil. It is obvious that the rate parameters valid for C-18 acids in rapeseed oil hydrogenation may not be the same as those valid for cottonseed oil or soybean oil hydrogenation owing to the absence of interfering acids in these oils. It should also be noted that the hydrogenation of

C-18 acids with various numbers of double bonds occurs in part simultaneously, so the parameters of these individual rate equations can not be estimated independently.

Objective Function

The objective function F to be minimized in determining the best set of parameters in the rate equation for C-18 acids may thus be written:

$$F = w_1(\hat{x}_1 - x_1)^2 + w_2(\hat{x}_2 - x_2)^2 + w_3(\hat{x}_3 - x_3)^2 \qquad \text{(I)}$$

where

w_1, w_2, w_3 = weights calculated as the inverse variance of x_1, x_2 and x_3 according to Hunter (8)

$\hat{x}_1, \hat{x}_2, \hat{x}_3$ = predicted weight fractions of C-18 acids with one, two, and three double bonds, respectively

x_1, x_2, x_3 = experimental weight fractions of C-18 acids.

The predicted weight fraction $\hat{x}_j$ (j = number of double bonds) is a function of the parameters to be calculated.

Rate Equation

The parameters are defined by the rate equation

$$-\frac{d\hat{x}_j}{dt} = k_j^o(K_H)^{\beta_j}\exp(-E_j/RT)\,(\hat{x}_j)^{\alpha_j}(p)^{\beta_j} \qquad \text{(II)}$$

where

k_j^o = pre-exponential factor of the rate constant

α_j,β_j = reaction orders

E_j = Arrhenius activation energy

p = hydrogen pressure corresponding to the hydrogen concentration at the surface of the catalyst. This concentration is equal to $K_H \cdot p$, where K_H is the hydrogen solubility constant.

The reaction order α_j was found to be independent of temperature and very close to unity in hydrogenation of cottonseed oil or rapeseed oil. On the other hand, β_j was dependent on the temperature and since this dependence was rather small, β_j was assumed to be a linear function of T, i.e., β_j may be written

$$\beta_j = a_j T + b_j \qquad \text{(III)}$$

where a_j and b_j are constants to be estimated. It should be noted that both α_j and β_j are assumed to be independent of the iodine value.

Influence of the Mass Transfer Steps

Since the hydrogen concentration at the surface of the catalyst and, subsequently also the corresponding hydrogen pressure p, are dependent on the mass transfer rate, p is calculated from the mass transfer equation given in (8)

$$p = p^o + (0.039\,\rho/K_H)\,[d(\text{I.V.})/dt]\,[(1/ka) + (1/k_H\,a_p)] \qquad \text{(IV)}$$

where

p^o = hydrogen pressure in the outlet gas

ρ = density of the oil

d(I.V.)/dt = change of iodine value/sec

ka = volumetric mass transfer coefficient for the hydrogen transport across the liquid film near the gas phase

$k_H\,a_p$ = volumetric mass transfer coefficient for the hydrogen transport across the liquid film near the outer surface of the catalyst.

The volumetric mass transfer coefficients are dependent on the mixing conditions in the reaction vessel. In laboratory studies under very intense mixing conditions these coefficients were estimated to be of the order of ka = 2 sec^{-1} and $k_H\,a_p$ = 3 sec^{-1} (8). Moreover, the hydrogen solubility constant was found to be

$$K_H = 0.0203\exp(-710/T)\ \text{mol/liter atm. (9),}$$

where T is the absolute temperature in Kelvin. The number 0.039 in eq. IV is a factor used to convert the reaction rate from iodine value sec^{-1} to mol hydrogen $(\text{liter oil})^{-1}\text{sec}^{-1}$. The density of the oil is ca. $\rho = 0.8$ kg/liter. The derivative d(I.V.)/dt in eq. IV is calculated after the fit of a polynomial of the third degree to the iodine values in each series by the method of least squares in a separate calculation routine.

Intercorrelation Between the Parameters

In order to obtain well-conditioned confidence regions of the pre-exponential factor k_j^o and the Arrhenius activation energy E_j, the rate constant $k_j = k_j^o\exp(-E_j/RT)$ was redefined in the following way (10)

$$k_j = k_j^{o\prime}\exp\left\{-\frac{E_j}{R}[(1/T) - (1/\bar{T})]\right\} \qquad \text{(V)}$$

where $\bar{T}$ is the average temperature of all hydrogenations. The original pre-exponential factor k_j^o is then calculated from

$$k_j^o = k_j^{o\prime}\exp\left\{(E_j/R)\,(1/\bar{T})\right\} \qquad \text{(VI)}$$

Integration Procedure

Integration of eq. II was performed in a special routine using a modified Runge-Kutta method, which makes use of variable step length.

Minimum Search Routine

The main problem in estimating the parameters of the mathematical model was to find a stable numerical multiparameter search which fits the model to the experimental results. Several minimum search methods are presented in the literature, and good reviews are given in (6). A special search method was developed for estimating the best set of parameters of the fat hydrogenation model. A short description of the search method is given here. The mathematical description may be found in (10).

Values of the fatty acid composition during the hydrogenation are calculated by integrating the rate equations with a starting set of E_j, $k_j^{o\prime}$, a_j, and b_j and with the parameter sets $E_j + \Delta E_j$, $k_j^{o\prime}$, a_j, and b_j, E_j, $k_j^{o\prime}$, $+ \Delta k_j$, a_j, and b_j, and so on, separately at every value of j, where j is the number of double bonds of the C-18 acid. The squared sums of differences between the predicted fatty acid content and the experimental one are calculated for each set of parameter values. At least one of these squares sums will be smaller than the squares sum obtained for the starting set of parameters. The new starting set of parameters will thus be that which gives the smallest squared sum.

In mathematical terms this means that the employed algorithm calculates the direction of steepest descent at the starting point. The second point in the direction of steepest descent is chosen very close to the starting point from which point a new direction of steepest descent is calculated. The search starts from the first point using its steepest descent modified with a second degree correction. The correction is calculated from the difference between the steepest descent in the two points.

The iterative search is very simple. The step length is divided by two when the difference in the object function evaluations changes sign.

TABLE I

Minimum Search Using the Test Function

$F(p_1, p_2) = 100(p_1^2 - p_2)^2 + (1 - p_1)^2$

Starting interation point: $p_1 = -1.25$, $p_2 = 1.00$

Iteration number	Number of function evaluations	p_1	p_2	F
0	0	-1.2500	1.0000	36.70313
1	24	-1.0422	1.0942	4.17696
4	78	-0.9095	0.8182	3.65442
7	135	-0.7120	0.4967	2.94128
10	187	-0.4933	0.2302	2.24702
13	247	-0.2369	0.0408	1.55351
16	300	0.0120	-0.0182	1.00989
20	376	0.2725	0.0589	0.55274
25	477	0.4809	0.2211	0.27984
30	574	0.6232	0.3815	0.14666
35	665	0.7239	0.5193	0.07851
40	770	0.8022	0.6402	0.04023
45	859	0.8636	0.7435	0.01911
50	953	0.9071	0.8213	0.00888
55	1058	0.9426	0.8875	0.00339
60	1168	0.9669	0.9343	0.00113
65	1274	0.9822	0.9644	0.00033
70	1380	0.9912	0.9823	0.00008
75	1488	0.9965	0.9929	0.00001
80	1604	0.9992	0.9984	0.00000
84	1716	1.0000	1.0000	0.00000

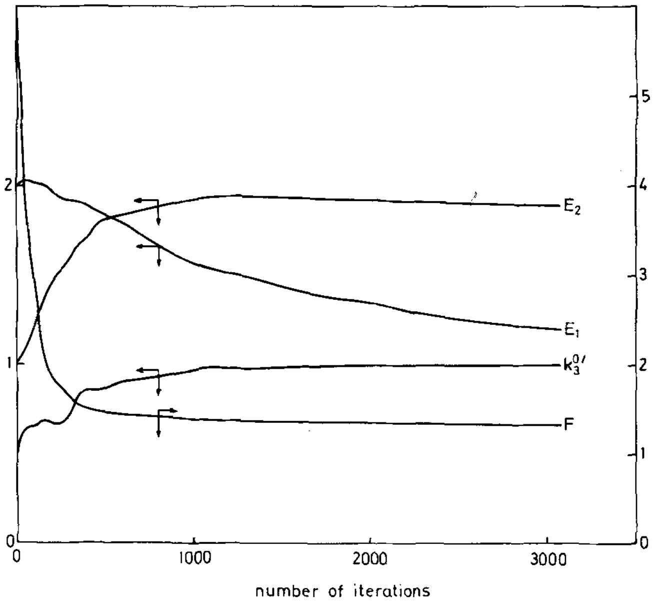

FIG. 1. Proceeding of activation energies (E_1, E_2), reparameterized pre-exponential factor ($k_3^{0\prime}$) and objective function (F) during an ordinary search for the best set of parameter values of rapeseed oil hydrogenation model. (Relative units on the ordinate.)

RESULT

Test of the Search Algorithm

In order to illustrate the way in which the algorithm works, the method was tested by a special test function, usually referred to as the Rosenbrock curved valley (6):

$$F(p_1,p_2) = 100\{p_1{}^2 - p_2\}^2 + \{1 - p_1\}^2 \qquad \text{(VII)}$$

where p_1 and p_2 are independent variables.

This function is often suggested as a test for numerical search methods because of the difficulty in finding the flat minimum situated at one end of a curved valley.

As suggested, the point $p_1 = 1.25$, $p_2 = 1.00$ was chosen as starting point for the test with the curved valley function. The minimum $F = 0$ is situated at the point $p = 1.0$, $p_2 = 1.0$.

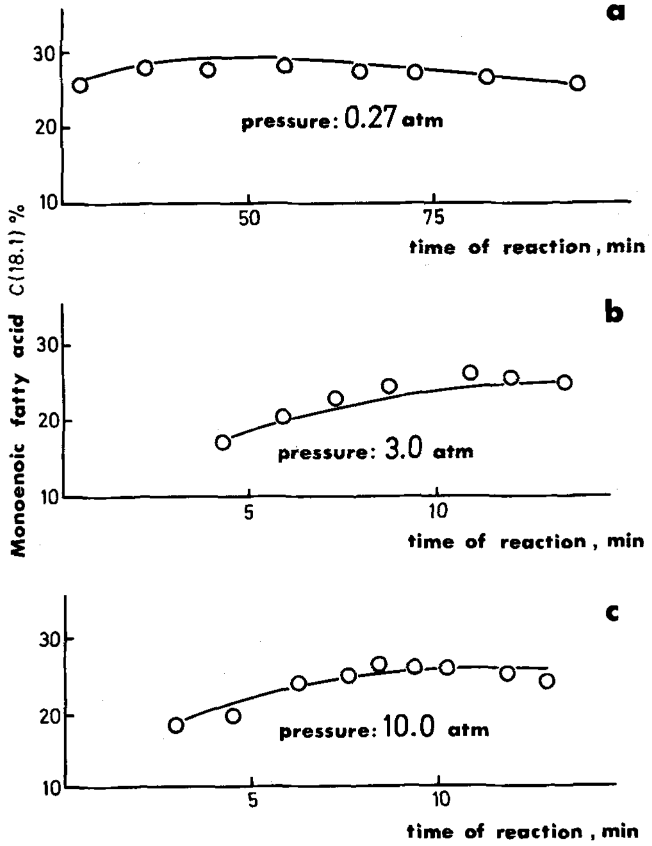

FIG. 2. Example of the agreement between predicted (——) and experimental (○) contents of monoenoic fatty acid C(18.1) in rapeseed oil at 180 C. The predicted values are based on seven hydrogenations at different pressures.

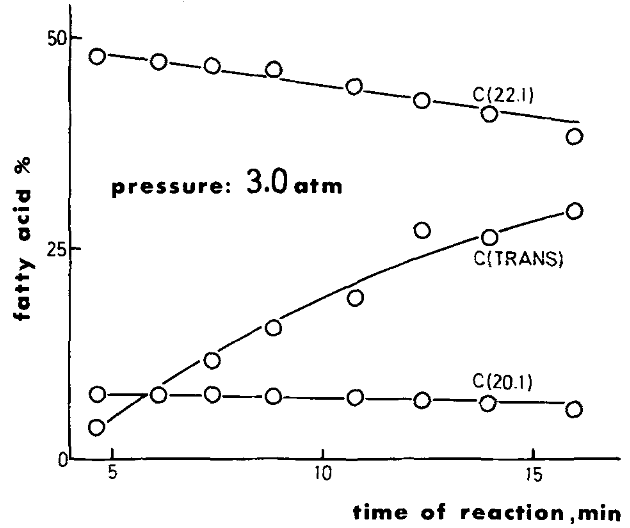

FIG. 3. Example of the agreement between predicted (——) and experimental (o) values of erucic acid, C(22.1), gadoleic acid, C(20.1), and total *trans* fatty acids, C(TRANS) in rapeseed oil hydrogenation at 180 C. The predicted values are based on seven hydrogenations at different pressures.

The present algorithm required 84 iterations to reach minimum. As can be seen in Table I, the search has a very stable performance even though it is relatively slow. For economic reasons high speed is usually desired. In this case, a preliminary study showed that rapid parameter estimation routines exhibited stability problems.

Illustration of the Computational Method on the Fat Hydrogenation Model

The fitting of the parameters in the mathematical model for the fat hydrogenation reactions is presented in greater detail in (7). The algorithm is very stable even when more than 10 parameters are included. As can be seen in ref. (9), a satisfactory model for the rapeseed oil hydrogenation reactions was computed using the algorithm.

The algorithm is illustrated here for one fit of the C(18)-reaction model. The model has twelve parameters. The changes in three of the parameters and the object function are given in Figure 1 as functions of the number of interactions. Similar to the test function, the performance is very stable. F is the function to be minimized and E_1 and E_2 are the activation energies in the hydrogenation of C(18.1) and C(18.2) acids, respectively. The indices stand for one and two double bonds. $k_j^{o\prime}$ is the redefined pre-exponential factor according to eq. VI for the hydrogenation of C(18.3).

Other examples of the fit of the same model with twelve parameters are given in Figures 2a-2c and in Figure 3. The predicted values are based on seven hydrogenations of rapeseed oil at 180 C and at various pressures between 0.27 atm and 10.0 atm. Figures 2a-2c show the agreement between predicted and experimental weight percent of monoenoic fatty acids with eighteen carbon atoms, C(18.1) and in Figure 3 the agreement between predicted and experimental values of erucic acid, C(22.1), gadoleic acid, C(20.1), and total *trans* fatty acids, C(TRANS), is given. Despite the fact that the predicted values are based on seven different hydrogenations at different pressures, the agreement between predicted and experimental values is good even for a single run. The agreement between the model and the experiment was statistically tested in ref. (8).

The entire algorithm is presented in ref. (10) or may be obtained from the author.

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