An Improved Model for Industrial Vegetable Oil Hydrogenation

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ABSTRACT

A simplified mathematical model has been used to describe industrial vegetable oil hydrogenation. The temperature dependence of the reaction rate constants is taken into account. Data collected from full-scale hydrogenation units are used to evaluate the model parameters. A simple technique is suggested for parameter estimation.

INTRODUCTION

Earlier it was shown that a simplified model for the hydrogenation reaction scheme adequately fits the plant data collected from several industrial units (1). Implicit in the parameter estimation scheme was the assumption of time-invariant reaction temperature. The assumption is violated often in practice, thus limiting the applicability of the model. The present work overcomes this drawback of the earlier model.

MATHEMATICAL MODEL

The simplified reaction scheme

$$L \xrightarrow{k_L} O \xrightarrow{k_O} S$$

where L, O, and S stand for linoleate, oleate, and stearate, respectively, was earlier found adequate to represent hydrogenation (1). This scheme and other features of the earlier model, such as hydrogen mass transfer from the gas phase to the liquid phase as the controlling step and nondistinction between *cis-trans* isomers of the fatty acid chains, have been retained in the present model. The reaction rate constants k_L and k_O are assumed to obey Arrhenius dependence on temperature.

$$k_L = k_L^O \exp(-E_L/R_gT) \quad [1]$$

$$k_O = k_O^O \exp(-E_O/R_gT) \quad [2]$$

where k^O and E are the preexponential factor and activation energy, respectively, and R_g and T are gas constant and reaction temperature. The rates of formation of linoleate and oleate are:

$$-R_L = k_L^O \exp(-E_L/R_gT)\,[L]\,p_{H_2}^a\,m \quad [3]$$

$$R_O = -R_L - k_O^O \exp(-E_O/R_gT)\,[O]\,p_{H_2}^b\,m \quad [4]$$

Nomenclature: a,b, hydrogen concentration power in rate expression; E, activation energy, kcal/kg mole; k_B, hydrogen mass transfer coefficient, kg mole sec^{-1} atm^{-1} (kg oil)$^{-1}$; k_L, reaction rate constant for linoleate hydrogenation, sec^{-1} $atm^{-0.5}$ (kg cat/100 kg oil)$^{-1}$; k_O, reaction rate constant for oleate hydrogenation, sec^{-1} atm^{-1} (kg cat/100 kg oil)$^{-1}$; k^0, preexponential factor, dimension same as corresponding k; [L], linoleate concentration, kg/100 kg oil; m, catalyst concentration, kg/100 kg oil; N, hydrogen mass transfer rate, sec^{-1} (kg mole/kg oil); [O], oleate concentration, kg/100 kg oil; P_{H_2}, hydrogen pressure in liquid phase, atm; $p^O_{H_2}$, hydrogen pressure in gas phase, atm; R, reaction rate, sec^{-1} (kg/100 kg oil); Rg, gas constant, kcal kg mole^{-1} K^{-1}; T, absolute temperature, K; T_{avg}, average temperature, K; Δt, time step, sec. Subscripts: L, linoleate; O, oleate.

where [L] and [O] are linoleate and oleate concentrations, p_{H_2} is the liquid phase hydrogen concentration, and m the catalyst concentration. a and b are chosen as 0.5 and 1.0, respectively (2). The liquid phase hydrogen concentration is given as:

$$p_{H_2} = p^O_{H_2} - N/k_B \quad [5]$$

$p^O_{H_2}$ being the gas phase hydrogen concentration. k_B is the mass transfer coefficient, and N is the hydrogen mass transfer rate given as:

$$N = -(R_O - 2R_L) \quad [6]$$

Equations 1-6 constitute the mathematical model. Linolenic acid, if present in the oil, is accounted for as discussed earlier (1). For the solution of this system of equations, the hydrogenation time is visualized as a series of small time steps, Δt, over each of which the following assumptions are valid: temperature is constant over each time step; the reaction rates R_L and R_O remain constant over the time step and are calculated using [L] and [O] values at the beginning of the time step.

These simplications are equivalent to the finite difference approximation of the differential Equations 3 and 4. The solution of the system of Equations 1-6 to obtain linoleic and oleic concentration profiles reduces to the repetitive application of the following sequence of calculation for the i^{th} step:

(1) Calculate temperature at i^{th} and $(i+1)^{th}$ node on the time scale. Calculate the average temperature, T_{avg}.

$$T_{avg} = (T_i + T_{i+1})/2 \quad [7]$$

(2) Assume a value for N (say N_{old}). It may be taken to to be equal to the value of N for the previous interval.

(3) Calculate P_{H_2} using Equation 5.

(4) Calculate R_L and R_O using T_{avg}, $[L]_i$, $[O]_i$, for T, [L], [O], respectively, in Equations 3-4.

(5) Calculate N (say N_{new}) from Equation 6.

(6) (a) If

$$\left|\frac{N_{new} - N_{old}}{N_{old}}\right| > \epsilon,$$

where ϵ is a specified tolerance, set $N = (N_{old} + N_{new})/2$ and repeat steps 3-5.

(b) If

$$\left|\frac{N_{new} - N_{old}}{N_{old}}\right| < \epsilon,$$

convergence criterion is satisfied. Calculate $[L]_{i+1}$, $[O]_{i+1}$ from the finite difference forms of R_L and R_O, namely:

$$R_L = \frac{[L]_{i+1} - [L]_i}{\Delta t}$$

$$R_O = \frac{[O]_{i+1} - [O]_i}{\Delta t}$$

The choice of the time step Δt is vital. By trial and error, a value of 1 min was found adequate.

PARAMETER ESTIMATION

During the hydrogenation of a batch, oil samples were collected and reaction temperature noted at suitable time intervals. The oil samples were analyzed for linoleate, oleate, and stearate concentrations. These discretized concentration and temperature profiles were sufficient to estimate the model parameters k_L^O, E_L, k_O^O, E_O, and k_B.

The calculation scheme described earlier can be used to simulate concentration/time profiles pertaining to a set of values of the parameters. A set which gives the best fit (least squares fit) between the simulated and plant data is the desired estimate of the parameters. Starting with an arbitrary guess for the parameter values, a suitable technique should be used to improve this guess and arrive at the best estimate in a few steps. The problem of parameter estimation is thus one of optimization where the parameters k_L^O, E_L, k_O^O, E_O, and k_B are the optimization variables, and the squared deviation is the objective function to be minimized. The problem was found appropriately posed for the use of complex procedure of Box as an optimization technique (3). To implement Box's procedure, constraints were imposed on the values the variables could take, k_L^O, E_L, k_O^O, E_O, and k_B were allowed to vary between 50 and 200% of their earlier estimates (1). These limits were found flexible enough to allow practically unconstrained optimization.

RESULTS AND DISCUSSION

Five different industrial hydrogenation plants working

TABLE I

Operating Conditions for Various Plants

Case	Oil hydrogenated	Batch size (tons)	Temperature range (C)	Average hydrogen pressure (atm)	Catalyst concentration (kg catalyst/ 100 kg oil)	Stirrer speed (rpm) and number of impellers	Hydrogenator type
I	Cottonseed	5.5	145–183	1.7	0.048	42 2	Gas recirculation
II	Soybean	5.5	165–210	1.68	0.048	42 2	Gas recirculation
III	Soybean	5.0	150–200	2.3	0.048	70 2	Dead end
IV	Soybean	5.5	155–200	2.4	0.045	–	Gas recirculation
V	Soybean	8.0	105–238	4.4	0.048	144 2	Gas recirculation

TABLE II

Comparison between Experimental Data and Calculated Results

Composition	Initial	After 60 min Exptl	After 60 min Calc	After 90 min Exptl	After 90 min Calc	After 120 min Exptl	After 120 min Calc	After 150 min Exptl	After 150 min Calc	After 180 min Exptl	After 180 min Calc	After 195 min Exptl	After 195 min Calc
Case I													
Linoleic	43.7	33.6	33.6	34.1	29.4	29.7	25.7	21.2[a]	20.3	–	–	–	–
Oleic	30.0	39.6	39.0	43.4	42.9	46.7	46.4	50.7[a]	50.8	–	–	–	–
Stearic	6.5	6.9	7.1	7.3	7.5	7.7	8.1	8.2[a]	9.1	–	–	–	–
Case II													
Linoleic	53.0	–	–	29.7	30.4	24.5	24.5	20.2	19.8	16.6	16.1	15.1	14.6
Oleic	30.5	–	–	53.3	52.5	58.3	58.1	62.3	62.5	65.6	65.8	67.0	67.1
Stearic	6.9	–	–	7.4	7.5	7.6	7.8	7.9	8.1	8.2	8.5	8.3	8.6
Case III													
Linoleic	50.8	29.7	30.5	22.7	22.8	17.4	16.9	13.3	12.4	9.7[b]	8.6	–	–
Oleic	31.2	51.8	50.9	58.4	58.2	63.3	63.6	67.0	67.5	70.7[b]	70.5	–	–
Stearic	5.3	5.8	5.8	6.2	6.3	6.6	6.8	7.0	7.4	7.6[b]	8.2	–	–
Case IV													
Linoleic	53.0	31.8	32.8	24.6	24.9	19.1	18.7	14.8	13.9	11.4	10.4	–	–
Oleic	30.5	51.5	50.3	58.2	57.8	63.5	63.6	67.5	67.7	70.5	70.7	–	–
Stearic	5.4	5.6	5.8	6.1	6.2	6.3	6.7	6.6	7.2	7.0	7.7	–	–
Case V													
Linoleic	53.0	28.9	30.7	21.4	20.7	15.8	13.2	11.6	8.1	–	–	–	–
Oleic	29.9	53.6	51.6	60.9	60.7	66.2	67.0	69.9	70.4	–	–	–	–
Stearic	4.8	5.2	5.4	5.4	6.3	5.7	7.6	6.2	9.1	–	–	–	–

[a]Data compared after 165 min.

[b]Data compared after 185 min.

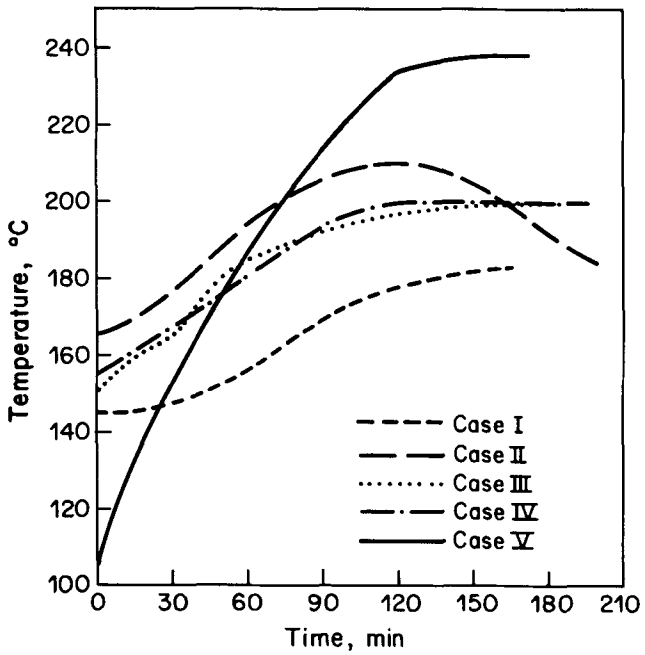

FIG. 1. Temperature variation during hydrogenation as a function of time.

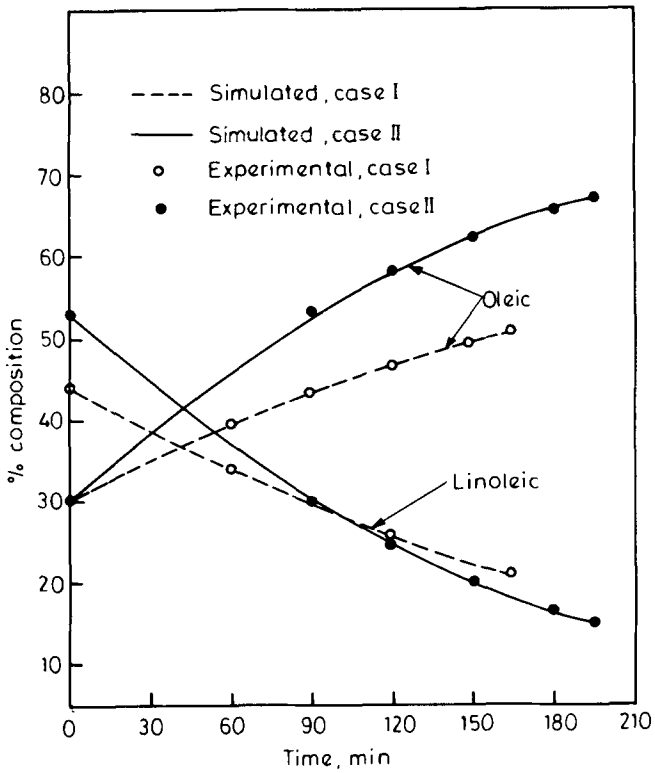

FIG. 2. Simulated and experimental composition profiles for oleic and linoleic acids.

under different operating conditions (see Table I) have been simulated using the present model. All the plants used 25% nickel on silica support as catalyst supplied by the same manufacturer. The calculation results for all these cases are presented in Table II. The calculated compositions are compared with experimentally measured values at certain intervals of hydrogenation time.

The temperature variation as a function of time for all the units is shown in Figure 1. As seen in this figure, the temperature varies over a wide range in all the cases investigated, and the use of an average constant temperature over the entire hydrogenation time would be too gross an assumption. The present model correctly accounts for this variation as evidenced by a close agreement between measured and calculated values of compositions at all times and for all the cases. The deviations are small, the maximum deviation for oleic acid concentration being less than 4% (case V). On the average, the calculated oleic concentration deviated from experimentally measured values by less than 1%. Deviations in linoleic acid concentration were somewhat larger but the greatest discrepancy almost always occurred at the end of the hydrogenation period where linoleic concentration was low. Error in the measurement of concentrations is likely to be large when measuring small quantities, resulting in larger deviations. For cases I and II, maximum linoleic concentration deviations were 4.5 and 2.5%, respectively. For the remaining cases, the maximum deviations were greater than 10%, primarily because of larger uncertainty in the experimentally measured values owing to low concentrations. Since stearic acid concentration is obtained by material balance, there is no additional information obtained in its comparison. Figure 2 shows a graphical comparison between the measured and calculated compositions for two typical cases (cases I and II).

Table III gives the estimated parameters k_L^O, E_L, k_O^O, E_O, and k_B for all five cases. As was discussed earlier (1), k_B values are likely to be different for different plants because of differences in speed of agitation, agitator-

TABLE III

Estimated Parameters

Case	Parameter				
	$k_L^O \times 10$	E_L	$k_O^O \times 10$	E_O	$k_B \times 10^6$
I	0.3374	2828.0	0.1726	4605.0	0.5527
II	0.4029	2878.0	0.0991	5215.0	1.2360
III	0.4116	2670.0	0.1799	5539.0	4.6820
IV	0.3747	2600.0	0.1556	5553.0	4.2454
V	0.3496	2614.0	0.1200	5362.0	4.9915

Dimensions: k_O^O sec^{-1} atm^{-1} (kg cat/100 kg oil)$^{-1}$; E_L k cal/kg mode; k_L^O sec^{-1} $atm^{-0.5}$ (kg cat/100 kg oil)$^{-1}$; E_O kcal/kg mole; k_B kg mole $(sec)^{-1}$ $(atm)^{-1}$ $(kg\ oil)^{-1}$.

sparger design, size and location of baffles, etc. The reaction kinetic parameters should be similar in all the cases since essentially the same reactions occur everywhere. As seen in Table III, these parameters are quite similar. However, owing to slight differences in the impurities present in the different cases, which do influence the reactions in a complex way, some deviations can be expected to be present.

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Improved Separation of Natural Oil Triglycerides by Liquid Chromatography Using Columns Packed with 3-µm Particles

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ABSTRACT

Very high-resolution separations of triglycerides in various natural oils have been demonstrated by liquid chromatography using short columns packed with 3-µm alkyl bonded-phase particles. Analysis times range from 8 to 16 min without prior sample clean-up. The primary detector used was a refractive index detector having low dispersive characteristics. Both the high efficiency of the columns and the selectivity of the 3-µm packing material contribute to the separation of several critical pairs of triglycerides. A substantial reduction in analysis time was also achieved. An ultraviolet detector operated at 220 nm was used to illustrate an alternative detection approach.

INTRODUCTION

The use of high-performance liquid chromatography (LC) for the separation of individual triglycerides present in fats and oils has been increasing in recent years. These analyses are important in the natural oil industry for process and product quality control purposes. Also, at the research/development level, detailed triglyceride data might facilitate the understanding of triglyceride biosynthesis and deposition in plants and animal cells (1).

The LC system most commonly employed in triglyceride analysis consists of an alkyl bonded-phase column and a refractive index detector. Although aqueous mobile phases are generally used with these columns, due to the lipophilicity of triglycerides, water cannot be used in the mobile phase for this particular application. Therefore the mobile phases generally employed consist of mixtures of acetone and acetonitrile, and occasionally tetrahydrofuran, methylene chloride or hexane. The conspicuous absence of water in the mobile phase, prompted the term nonaqueous reversed-phase or NARP to describe the above system.

El-Handy et al. (1-2) and Plattner (3) have reported quite extensively on column and mobile phase selectivities in triglyceride separations. Jansen (4) has studied the effect of low temperature and Lie Ken and Jie (5) have investigated several quantitative aspects of triglyceride analysis. Parris (6) and Payne-Wahl et al. (7) have shown the utility of an infrared detector and gradient elution in triglyceride separation. The latter group has also demonstrated the capability of analyzing free acids, mono-, di- and triglycerides in a single assay (7). Various natural oils have been studied in some detail using NARP chromatography, including oils from palm (1,9), olive (4,10), peanut butter (8), soybean (1,3,7), coconut (2,9), corn (1), rapeseed (9), and cocoa butter (9).

Recent advances in column and instrument technology have significantly enhanced LC performance in recent years (11,12). We have previously reported the separation on many important food constituents in 1-3 min using short, small-particle columns (13,14). The aim of this study is to demonstrate the utility of this improved LC system in triglyceride separations.

EXPERIMENTAL

Reagents

Triglyceride standards were of the highest purity grade purchased from Supelco, Inc. (Bellefonte, PA) and Sigma Chemical Co. (St. Louis, MO). HPLC-grade acetonitrile, acetone and tetrahydrofuran (THF) were obtained from Fisher Scientific (Pittsburgh, PA). Natural oil samples were purchased at the open market in Connecticut. The palm olein sample was obtained from sources within the industry.

Columns

The LC columns used in this study were Perkin-Elmer HS-3 high-speed columns packed with 3-µm C_{18} bonded-phase particles. Dimensions of the columns are 100 X 4.6 mm id with a column void-volume of ca. 0.8 mL and efficiencies in the range of 13,000-15,000 theoretical plates measured under optimized conditions. Details on important column characteristics are available elsewhere (11,15). Because of the low column void-volume and high-efficiency, the resultant peak volumes are typically only 25-100 µL. Therefore, extra-column band broadening from injector, connecting tubing and detector must be minimized to preserve column performance (12). Several Perkin-Elmer HS-5 C_{18} columns (125 X 4.6 mm id) packed with 5-µm particles were also used; however, due to differences in packing selectivity, separation of critical triglyceride pairs were, in general, not satisfactory with these columns.