Technical

A Simulation Study of Industrial Vegetable Oil Hydrogenation Reactors

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ABSTRACT

A mathematical model has been developed to predict the course of industrial vegetable oil hydrogenation reactors. The model assumes that the reaction is mass-transfer-controlled. Suitable empirical equations have been used to describe rate of hydrogenation in preference over a mechanistic approach. The agreement between theoretical predictions from the model and plant data is generally satisfactory. Temperature, pressure and agitation intensity have strong effect on the kinetics of the reaction and on selectivity ratio under conditions of industrial reactors. The product quality is determined by overall selectivity which is governed by operating conditions, as well as the catalyst selectivity.

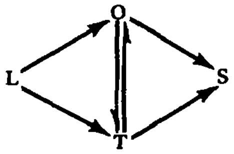
NOMENCLATURE

a,b: reaction order; k_1,k_2: pseudo-first order rate constants; k_B: mass transfer coefficient for hydrogen transfer across the gas-liquid interface, kg mol $s^{-1}atm^{-1}$ (kg of reaction mixture)$^{-1}$; k_L: rate constant of hydrogenation of dienoic acid to monoenoic acid in glycerides, $s^{-1}atm^{-1}$ (kg catalyst/100 kg liquid); k_O: rate constant for hydrogenation of monoenoic acid in glycerides, $s^{-1}atm^{-1}$ (kg catalyst/100 kg liquid); [L]: concentration of C-18 dienoic acid in glycerides, kg/100 kg oil; m: catalyst load, kg catalyst/100 kg liquid; N: rate of hydrogen transfer, kg mol H_2 (kg reaction mixture)$^{-1}s^{-1}$; [O]: concentration of C-18 monoenoic acid in glycerides, kg/100 kg oil; $p^o_{H_2}$: hydrogen pressure in gas phase, atm; p_{H_2}: equilibrium hydrogen pressure corresponding to hydrogen concentration at the catalyst surface, atm. Subscripts: H_2, hydrogen; L, linoleic acid; O, oleic acid.

INTRODUCTION

Partial hydrogenation of vegetable oils is an important industrial reaction and is usually done in batch-type slurry reactors involving solid catalyst, liquid oil and hydrogen gas phases. This reaction belongs to the class usually termed "complex reactions" which requires that the yield of a specific reaction product be selectively maximized rather than maximizing the overall conversion of the reactant(s). An attempt to design the reactor for maximal yield of the desired product, oleic acid in this case, will involve proper evaluation of the effect of mass transfer on the kinetics of the hydrogenation reaction and on the nature of the product distribution.

In cottonseed oil hydrogenation, the following scheme has been found (1,2) to satisfactorily represent the reactions:



[I]

where L = linoleic acid, O = oleic acid (*cis*), T = oleic acid (*trans*) and S = stearic acid. Ignoring isomerization, the reaction can be simplified to (3):

$$L \xrightarrow{k_1} (O + T) \xrightarrow{k_2} S, \qquad [II]$$

where k_1,k_2 = pseudo-first order rate constants.

The reaction scheme represented by Equation II was considered for the development of a kinetic model to predict the rate of formation of linoleic, oleic and stearic acids in glycerides. *Cis* and *trans* isomers of oleic acid were not considered separately. Moreover, separation of *cis* and *trans* isomers was not possible on the gas liquid chromatograph, which was used to obtain experimental concentration profiles.

Two different approaches have been used in the past for modeling the kinetics of hydrogenation in slurry reactors. Phil and Schoon (3) have reported the use of a power law model, whereas others (1,2) considered the Langmuir-Hinshelwood (L-H) model based on a proposed mechanism. In all cases, the authors validated their proposed models on the basis of laboratory-scale reactor data. The power law model is the easiest for fitting experimental data, but it does not take into account the mechanistic aspects of adsorption and surface reaction. The L-H model considers the reaction from mechanistic aspects, but contains too many parameters which makes it difficult to apply to industrial reactors with commercial catalysts.

Under the prevailing industrial practice, factors such as temperature and pressure vary throughout a batch, and the state of refined oil varies among batches (and therefore the activity and selectivity of the catalyst varies). It was considered desirable, therefore, to select a power law approach for this study.

THE MODEL

The hydrogenation reaction occurs on the catalyst surface and also inside its pores where linoleic acid is transported from the liquid phase and hydrogen is transported from the gas phase through the liquid. In order to develop a suitable mathematical model, one must consider all the transfer steps which determine the kinetics under the conditions prevailing in industrial units. However, it has been found (4) that, in commercial hydrogenation units, kinetics are controlled by mass transfer resistances, the controlling step being that of the transfer of hydrogen from the gas phase to the liquid phase. An order of magnitude analysis of resis-

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tances to transfer of hydrogen from gas to liquid, from liquid to catalyst surface, and total resistance of reaction, confirms the validity of the statement. The rate equations used are empirical:

$$-R_L = k_L\,[L]\,p^a_{H_2}\,m, \qquad [III]$$

$$R_O = (k_L\,[L]\,p^a_{H_2} - k_O\,[O]\,p^b_{H_2})m, \qquad [IV]$$

where k_L and k_O are rate constants; [L], [O] are linoleic and oleic concentrations, respectively; p_{H_2} = hydrogen pressure on the catalyst surface; m = catalyst load; R_L = rate of linoleic hydrogenation; R_O = rate of oleic formation; and a and b are empirical constants.

The value of exponents a and b of the hydrogen concentration in the liquid phase were taken to be 0.5 and 1.0, respectively, in view of the findings reported by Hashimoto et al. (2). The hydrogen transfer rate, N, from gas to liquid phase is given by:

$$N = k_B(p^o_{H_2} - p_{H_2}) \qquad [V]$$

where k_B = gas-to-liquid hydrogen mass transfer coefficient, and $p^o_{H_2}$ = hydrogen pressure in the gas phase.

The hydrogen consumed in the reaction is also equal to N, and is given by:

$$N = -(R_O + 2R_L) \qquad [VI]$$

Equations III-VI constitute the mathematical model for partial hydrogenation of vegetable oils. For a given set of parameters k_L, k_O, and k_B, the solution of the above system of equations yields the concentration vs time profiles of linoleate, oleate, stearate and hydrogen. It can be seen that these equations are coupled and the calculations of rate of formation of linoleate and oleate (i.e., R_L and R_O) involve p_{H_2}. The p_{H_2} can be calculated from Equation V if N is known; however, N is obtainable from R_L and R_O. As a consequence, the solution of Equations III-VI is necessarily iterative in nature. A simple iterative scheme used in this work is given in the next paragraph.

An initial guess for the hydrogen concentration in the liquid phase, p_{H_2}, when substituted in Equations III and IV provide the values for R_L and R_O. These, along with Equation VI, yield an estimate of N. The same guess for p_{H_2}, when used with Equation V, offers another estimate of N. If the difference between these 2 estimates is within preassigned tolerance limits, the p_{H_2} guess is adequate. Any significant difference between the 2 estimates of N is used to correct the guess for the p_{H_2} value. The Regula-Falsi procedure has been used in this study to reach the convergence on p_{H_2}.

ESTIMATION OF PARAMETERS

For the estimation of the kinetic parameters, k_L and k_O, experimental hydrogenation data are necessary. The hydrogen mass transfer coefficient (k_B) can, however, be calculated if the design of the reactor and agitator assembly plus the necessary physical properties of the oil-catalyst slurry are known. Suitable correlations exist for this purpose in the literature (5-9). For the case in which agitation is provided only by bubbling the hydrogen in the reactor, it is still possible to correlate the mass transfer coefficient to various design parameters (10,11). However, because of lack of available data from industrial plants, this approach could not be adopted in our study. k_B, like k_L and k_O, was estimated from hydrogenation data. Though different procedures can perhaps be considered to evaluate these parameters from plant hydrogenation data, the following iterative scheme was used and found to be computationally reasonable and efficient: (a) initial guess for the average value of liquid phase hydrogen concentration, p_{H_2}, is made over the hydrogenation time. (b) In terms of the pseudo-first order rate constants, k_1 and k_2 (Equation II), the rate of formation of linoleate and oleate can be written as:

$$-R_L = k_1\,[L] \qquad [VII]$$

$$R_O = k_1\,[L] - k_2\,[O] \qquad [VIII]$$

The linoleate and oleate concentration vs time data is used to obtain R_L and R_O, and thus estimate k_1 and k_2. (c) Utilizing the fact that, in our model, $k_1 = k_L p^{0.5}_{H_2} m$ and $k_2 = k_O p_{H_2} m$, the guessed values of p_{H_2} are used along with k_1 and k_2 values to get an estimate of k_L and k_O. The R_L and R_O values calculated from plant data are used in Equation VI to get a value of N. This, when substituted into Equation V along with p_{H_2}, gives an estimate of k_B. Thus, for any guess of p_{H_2}, estimates of k_L, k_O, and k_B are obtained. (d) These estimates of k_L, k_O and k_B are used in the simulation model based on Equations III-VI to develop linoleate, oleate and hydrogen concentration-time data, using the technique described earlier. The p_{H_2} vs time profile obtained is used to calculate average value of p_{H_2}. (e) The average value of p_{H_2} obtained above is compared with the earlier guess. If both values are within a preassigned tolerance limit, the convergence is said to be achieved, and k_L, k_O and k_B values corresponding to p_{H_2} are the desired estimates. If the difference between these 2 p_{H_2} values is large, this difference itself is used to obtain an improved guess for p_{H_2}. Steps c-e are repeated with the new value of p_{H_2}.

The initial and final compositions of oil for a particular batch, along with the batch time, are sufficient to estimate parameters k_L, k_O and k_B. These values are used to calculate concentration vs time profiles for linoleate and oleate using the simulation model. The simulated profiles are then compared to the experimental profiles. k_L and k_O values obtained at 2 different temperatures are given in Table I.

TABLE I

Rate Constants in Equations III and IV

Temperature (C)	$k_L \cdot 10^4$	$k_O \cdot 10^4$
165	15.30	0.299
195	22.36	0.340

As expected, it has been found that k_L and k_O values need be evaluated only once for a given catalyst. As all the plants whose data were used in this study used the same catalyst, the same values of k_L and k_O as reported in Table I were used. This is, however, not true of the mass transfer coefficient, k_B, which depends on many factors such as agitator-sparger design, size and location of baffles, speed of agitator and physical properties of the oil-catalyst-H_2 slurry. It was therefore necessary to calculate separate k_B values for each plant.

RESULTS AND DISCUSSION

Typical compositions of cottonseed and soybean oils from the beginning to the end of partial hydrogenation are given in Tables II and III. The esters of myristic, palmitic, linoleic, oleic and stearic acids are the components in cottonseed oil and the linolenic acid is the additional component present in soybean oil. The C-14 and C-16 saturated acids, as their compositions show, are unchanged during the reac-

TABLE II

Composition of Industrially Hydrogenated Cottonseed Oil: 5-Ton Batch[a]

Hydrogenation time (min)	Myristic, 14:0 (%)	Palmitic, 16:0 (%)	Stearic, 18:0 (%)	Oleic, 18:1 (%)	Linoleic, 18:2 (%)
0	0.62	19.3	6.4	30.0	43.7
45	0.99	22.1	5.4	36.3	34.2
60	1.00	22.5	5.8	39.1	31.4
75	0.73	22.5	5.7	40.3	30.7
90	0.99	21.3	6.5	41.4	29.8
105	0.89	21.2	5.8	42.8	28.7
165	0.84	20.6	7.9	48.9	20.9

[a] Hydrogen pressure, 1.7 atm; temperature of hydrogenation, 165 C.

TABLE III

Composition of Industrially Hydrogenated Soybean Oil: 5-Ton Batch[a]

Hydrogenation time (min)	Palmitic, 16:0 (%)	Stearic, 18:0 (%)	Oleic, 18:1 (%)	Linoleic, 18:2 (%)	Linolenic, 18:3 (%)
0	13.6	6.0	31.2	42.8	5.3
30	13.5	5.2	36.3	41.3	3.5
60	14.5	6.0	45.3	35.9	1.2
90	15.0	5.5	55.3	24.2	–
135	14.2	6.0	67.2	12.7	–
175	12.3	7.1	69.4	12.2	–
185	12.4	7.6	70.3	9.7	–

[a] Hydrogen pressure, 2.3 atm; temperature of hydrogenation, 190 C.

tion. Linolenic acid is present in small quantities compared to linoleic and oleic acids and reacts out fast compared to the total time of the reaction (Table III). Therefore, linolenic selectivity is not considered in this model.

Figures 1-5 give simulation results along with experimental, smoothed data for 5 different industrial cases working under different conditions of temperature (165-195 C), hydrogen pressure (1.7-4.4 atm), agitator speed (0-140 rpm), and catalyst concentrations (0.03-0.05%). Operating conditions for all these cases are given in Table IV. Although there was a wide variation in temperature during the course of reaction, an average temperature was calculated and used in this study. Compositions of linoleic, oleic and stearic esters are predicted from the present model along with the iodine value of the oil. The experimental values of different esters reported in the figures were obtained from the GLC analyses of the samples drawn at different times from the hydrogenators. The linolenic acid present in initial samples was added to linoleic acid using the relation, L = 1.5104 Ln, based on iodine values (L = linoleic acid concentration and Ln = linolenic acid concentration). The iodine values (IV) were determined by Wij's method and were checked with GLC analyses at a few points. The individual cases are discussed next.

Case 1 represents a partial hydrogenation of cottonseed oil. The temperature of the batch was low (165 C) which markedly lowered the rate of reaction as well as the selectivity ratio. The calculated values are found to match quite well within the experimental error, the maximal discrepancy being for stearic acid (Fig. 1).

Case 2 gives data for hydrogenation of soybean oil from the same plant as in case 1. The operating temperature was 190 C, which is relatively high. This is reflected in a higher rate of reaction and a much higher selectivity ratio. Here the simulated results agree very well with experimental values (Fig. 2).

Figure 3 represents data for another plant in which batch size and operating temperature were the same as in case 2. However, the operating pressure (2.3 atm) was about 35% higher than in case 2, and the agitator speed (70

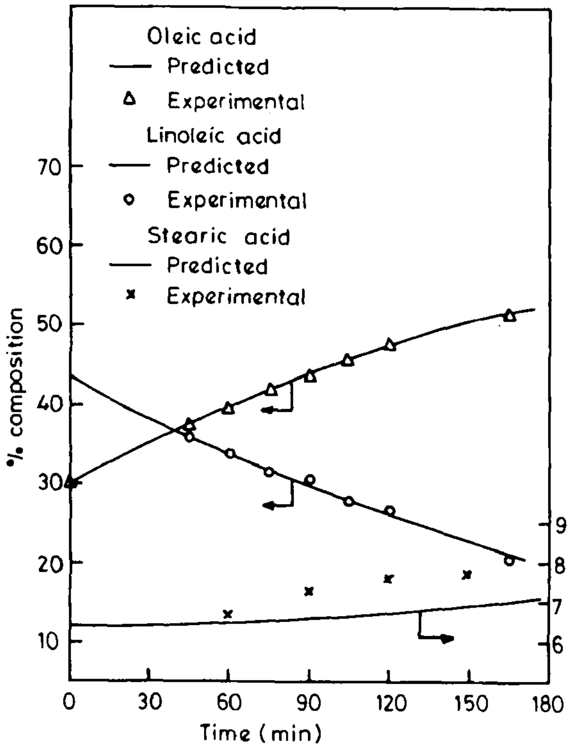

FIG. 1. Simulated and experimental composition profiles for oleic, linoleic and stearic acids for case 1.

TABLE IV

Operating Conditions for Different Plants (Case 1 to Case 5)

Batches studied in the same/different plants	Oil hydrogenated	Batch size (tons)	Ave. reaction temperature (C)	Ave. hydrogen pressure (atm)	Catalyst conc (%)	Stirrer speed (rpm) / No. of impellers	Hydrogenator type
Case 1	Cottonseed	5.5	165	1.7	0.048	42/2	Gas recirculation
Case 2	Soybean	5.5	195	1.68	0.048	42/2	Gas recirculation
Case 3	Soybean	5.0	190	2.3	0.048	70/2	Dead-end
Case 4	Soybean	5.5	195	2.4	0.045	–	Gas recirculation
Case 5	Soybean	8.0	195	4.4	0.048	144/2	Gas recirculation

rpm) was also much higher, resulting in a higher rate of reaction. The agreement between experimental and calculated compositions is quite good for this case, also.

Case 4 represents data for another plant with batch size 5.5 tons, the same operating temperature (190 C) as in cases 2 and 3, and almost the same operating pressure (2.4 atm). There was no agitation during the reaction which resulted in a lower mass transfer rate and, hence, lower rate of hydrogenation. The agreement between the experimental and calculated compositions is good (Fig. 4).

Figure 5 shows data for yet another plant of batch size 8 tons. The operating temperature was 195 C, as in case 2. Pressure was much higher as compared to other plants (4.4 atm), and the agitator speed was also very high (144 rpm). The reaction rate, under these conditions, is found to be 10% faster than in case 3, and 40% faster than in case 2, based on drop in IV. There is good match between predictions and plant data for linoleic and oleic acid esters; however, the predicted values for stearic acid are too high. The selectivity ratio (SR) is unexpectedly high, although the operating conditions were not favorable for high SR. This might be due to totally different plant practices prevailing there, compared to other plants. This is the only plant at which all processes other than hydrogenation are continuous. Continuous refining, in which centrifuges are used for soapstock removal, is known to reduce the soapstock and moisture content in the refined oil to much lower levels than in batch refining (10). This leads to a reduction in induction period and an increase in catalyst selectivity.

For all the cases considered, the calculated values for oleic and linoleic esters are within 5% of the experimental data points along the entire duration of reaction time. Moreover, the error is randomly distributed, which validates the model.

Pore diffusion is not important, and this resistance has been neglected in the present study. The poisoning effect of the catalyst is extremely difficult to account for, because that would require identification of different poisons and the rate data, which are not available. However, if it were considered in the model, it would enable the use of the total amount of catalyst rather than only the amount of the fresh catalyst, as taken into consideration in this study. Furthermore, the intrinsic selectivity of the catalyst is markedly affected by the poisons and, hence, depends on the refining and bleaching of the oil and the purification

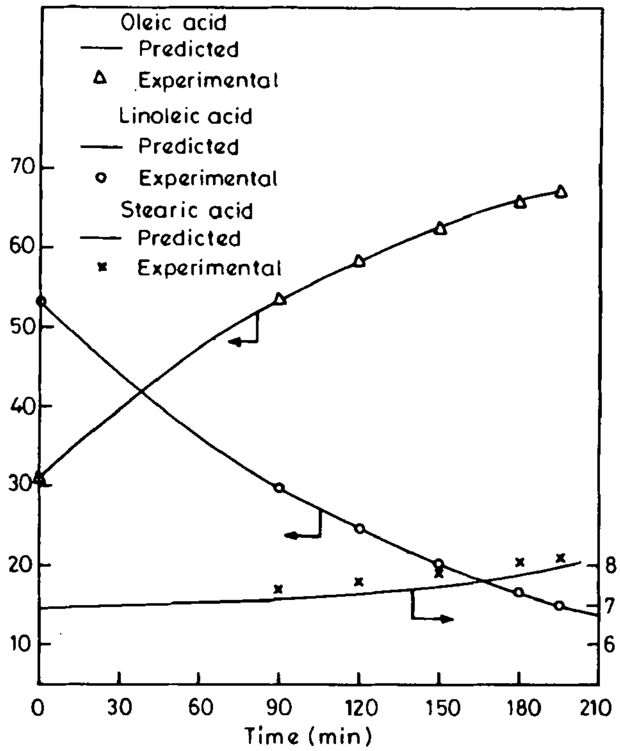

FIG. 2. Simulated and experimental composition profiles for oleic, linoleic and stearic acids for case 2.

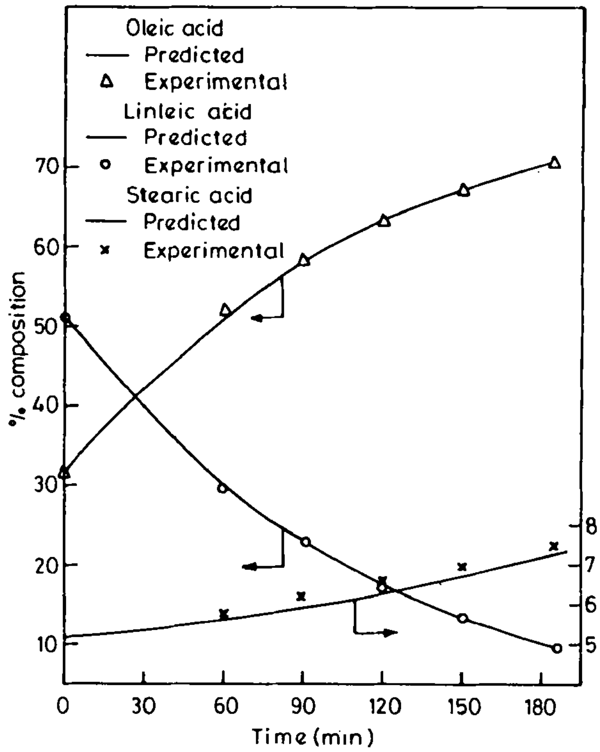

FIG. 3. Simulated and experimental composition profiles for oleic, linoleic and stearic acids for case 3.

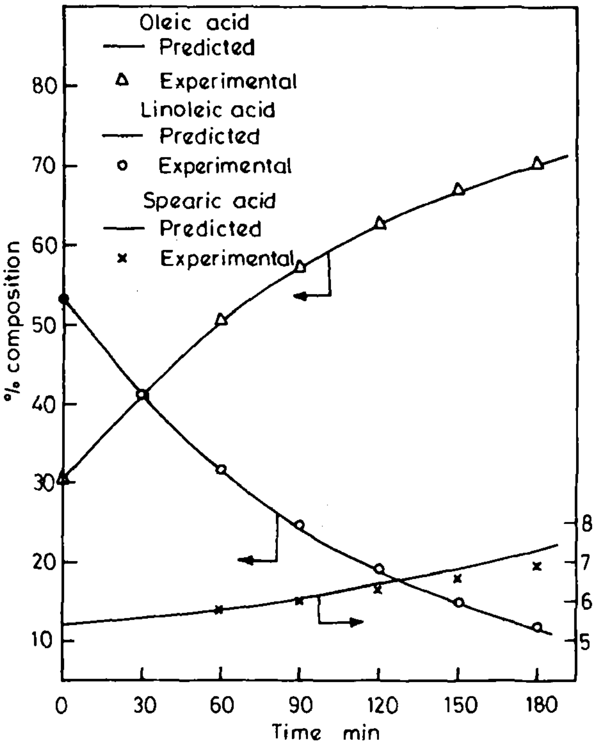

FIG. 4. Simulated and experimental composition profiles for oleic, linoleic and stearic acids for case 4.

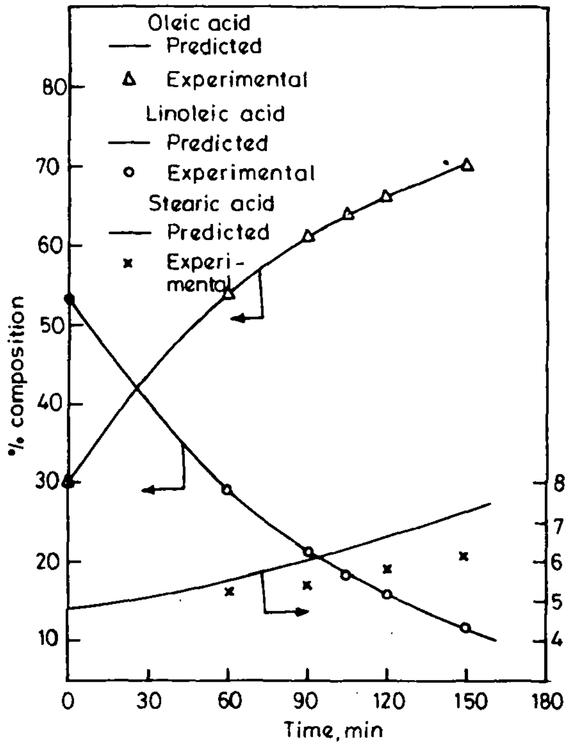

FIG. 5. Simulated and experimental composition profiles for oleic, linoleic and stearic acids for case 5.

step for hydrogen. Ignoring these factors effectively modifies the rate constants and the exponents in this model.

The proposed model is also likely to be influenced by the factors that determine the overall mass transfer coefficient. These factors include liquid phase solute diffusivity, continuous phase viscosity and the gas-liquid interfacial resistance (Hindustan Lever, Ltd., private communication). The diffusivity varies with ionic strength and with concentration of solutes which also change the solution viscosity (12). These effects could not be explained because of nonavailability of data from the plants.

The power law model used for describing the kinetics of partial hydrogenation of vegetable oils seems to be able to predict the course of reaction fairly well, despite its oversimplified approach. In commercial batch hydrogenators, mass transfer of hydrogen from the gas to liquid phase is the controlling resistance. All the plants included in this study used Hindustan Lever's Hycat, a silica-supported nickel catalyst (25% nickel), and, as such, the validity of rate constants over catalysts of other makes should not be assumed.

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