• Technical

Kinetics of the Hydrogenation of Rapeseed Oil: II. Rate Equations of Chemical Reactions

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ABSTRACT

The kinetics of rapeseed oil hydrogenation was studied at 140-220 C and at 0.3-10 atm hydrogen pressure in a laboratory reactor in the presence of 0.05% nickel catalyst. A mathematical model was fitted to the experimental data, and temperature and pressure dependence of the different reaction steps was discussed on the basis of the model. The adequacy of the model was tested by means of a residual analysis.

INTRODUCTION

Many kinetic studies have been carried out on hydrogenation of vegetable oils. Most of them deal with cottonseed oil and soybean oil, and only a few are concerned with rapeseed oil. Due to the very extensive literature on fat hydrogenation kinetics, only articles related to mathematical models of interest for simulation of the industrial process will be given in this literature survey. Before the computer era, Coenen (1), Eldib and Albright (2), and Wisniak and Albright (3) carried out extensive kinetic work on hydrogenation of different vegetable oils. More recently, mathematical modeling on fat hydrogenation kinetics was carried out by Albright and Wisniak (4), Albright, Allen, and Moore (5), Hashimoto, Muroyama, and Nagata (6), Hashimoto, Teramoto, and Nagata (7), Pihl and Schöön (8), and Hertzberg and Asbjørnsen (9).

In the present study, the kinetic behavior of the rapeseed oil hydrogenation is described with a mathematical model which takes into consideration the external mass transport steps. The influence of these steps was studied in part 1 of this study. The scale up and optimization studies will be given in forthcoming articles.

EXPERIMENTAL PROCEDURES

Material

The hydrogenations were carried out with rapeseed oil with a high content of erucic acid. The oil was bleached with Fuller's earth and heated under vacuum to remove water. The fatty acid composition of the triglycerides (% by wt) was 3.5% palmitic acid, 0.9% stearic acid, 12.1% oleic acid, 14.3% linoleic acid, 9.7% linolenic acid, 8% gadoleic acid (*cis*-9-eicosenic acid), and 48.4% erucic acid (*cis*-13-docosenoic acid). The catalyst was a commercial nickel-on-kieselguhr catalyst. The properties of the catalyst are given in part 1 of this investigation. The hydrogen gas was of high quality with low content of carbon monoxide. The gas was further purified by passing it through a molecular sieve and activated carbon.

Reactor and Performance of the Experiment

The reactor and the experimental conditions referring to the mixing of the slurry are given in part 1. All hydrogenations were carried out at a catalyst loading of 0.05% nickel. Hydrogenations at various catalyst loading would complicate the study because the rates of hydrogenation are not proportional to this loading.

Twenty-seven runs were carried out at 5 different temperatures between 140 and 220 C, and at 7 different pressures between 0.3 and 10 atm. The hydrogenations at the lowest pressures were carried out at reduced total pressure without addition of an inert gas. In each run 12 to 18 samples were taken from the reactor for analysis.

Analytical methods

The fatty acid composition was determined on a Perkin-Elmer 900 gas chromatograph. The glycerides were converted to methyl esters before the analysis. The content of isolated *trans* double bonds was determined spectrophotometrically at the wave number 970 cm^{-1} using a Perkin-Elmer Infracord. The iodine value (IV) was calculated from the gas liquid chromatographic (GLC) determination.

Mathematical Model of Chemical Reactions

The hydrogenation reactions occurring in rapeseed oil may be written in the following way

$$C(i.j) + H_2 \rightarrow C(i.j\text{-}1) \qquad (I)$$

where C(i.j) is the fatty acid in glycerides with i carbon atoms and j double bonds. Fatty acid with i = 18, 20, 22 and j = 1, 2, 3 are present in rapeseed oil. Three double bonds were present only in fatty acids with 18 carbon atoms. In equation (I), reactions with *trans* isomers are not included. So called shunt reactions, where the fatty acid C(i.j) is hydrogenated directly to C(i.j-2), are also omitted. Due to the difficulty in determining the individual *trans* isomers separately, the formation and reaction of *trans* isomers may be written

$$C(\mathit{cis}) + H_2 \rightarrow C(\mathit{trans}) \qquad (II)$$

$$C(\mathit{trans}) + H_2 \rightarrow C(\mathit{cis}) + C(\text{saturated}) \qquad (III)$$

where C(*cis*) is the sum of all unsaturated fatty acids minus the unsaturated acids in *trans* form. The mathematical model does not include the *cis-trans* isomerizations. These reactions cannot be described by equations (II) and (III). Because the rate equations are intended for process calculations and not for mechanistic interpretations, the rates of reaction were written as power type equations

$$r_{ij} = k_{ij}(x_{ij})^{\alpha_{ij}} (c_H)^{\beta_{ij}} \qquad (IV)$$

where r_{ij} is the rate of hydrogenation of the fatty acid C(i.j) in glycerides, and x_{ij} is the % by wt of the fatty acid in question; k_{ij} is the temperature dependent rate constant assumed to be of the form

$$k_{ij} = k^{o}_{ij} \exp(-E_{ij}/RT) \qquad (V)$$

where k^{o}_{ij} is the pre-exponential factor, and E_{ij} is the Arrhenius activation energy. As in many hydrogenations, the reaction order β_{ij} is assumed to be temperature dependent. Because the temperature dependence is assumed to be rather small, the reaction order may be written as a linear

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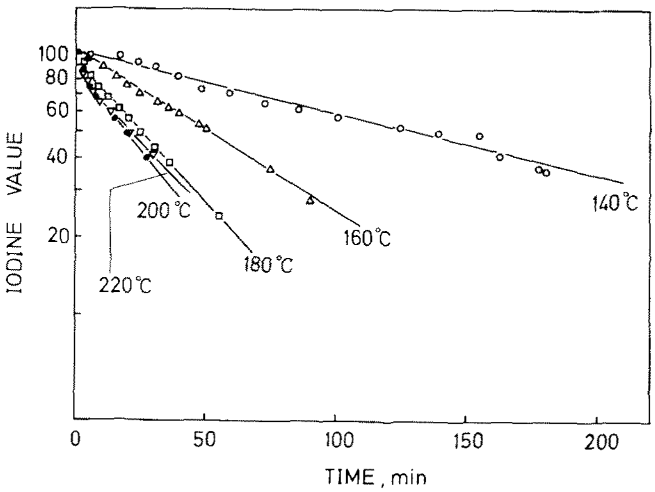

FIG. 1. Rapeseed oil hydrogenation at different temperatures; $p^o = 1.2$ atm.

relationship of the absolute temperature T. Moreover, the reaction order β_{ij} was assumed to be independent of the IV during the hydrogenation. The reaction order α_{ij} was assumed to be independent of both temperature and IV. The rate equations for reactions (II) and (III) may be written in a form similar to equation (IV), where the indicies "i" and "j" are replaced by *cis* and *trans*.

In fat hydrogenation kinetics, it is often convenient to correlate the reaction rate to the hydrogen pressure instead of the hydrogen concentration. By introducing the hydrogen pressure p, which corresponds to the hydrogen concentration c_H calculated from the equilibrium relationship

$$c_H = K_H p, \qquad \text{(VI)}$$

where

$$K_H = K_H^o \exp(-\Delta H/RT), \qquad \text{(VII)}$$

the rate equation (IV) may be written

$$r_{ij} = k_{ij}(K_H)^{\beta_{ij}}(x_{ij})^{\alpha_{ij}}p^{\beta_{ij}} \qquad \text{(VIII)}$$

Methods of Mathematical Treatment

The values of the exponents and the constants in the rate equations were estimated by the method of least squares. The minimum search included in this method was carried out on a digital computer (IBM 360/65) using a method by Bern (unpublished data) especially designed for this type of kinetic problems. To reduce the correlation between the pre-exponential factor and the apparent activation energy, the rate constant was redefined (10). All data concerning the C-18 system were used simultaneously in the estimation of the parameters. The variance of the experimental values of the various fatty acids of the C-18 system is quite different, so wt factors were introduced into the calculation in accordance with Hunter (11). No variation of these wt factors was found necessary. Because the C-22, the C-20, and the *cis-trans* systems are not coupled to the C-18 system in the proposed model, the parameters of these rate equations could be estimated separately. No wt factors were introduced in this calculation. In all calculations, the variance of the experimental values was assumed to be low in comparison to the variance of predicted values. The pressure p, corresponding to the concentration c_H at the external surface of the catalyst, was calculated from the gas pressure p^o of the outlet by correction for the external transport resistance, as given by equation IX in part 1 of this study. The derivative d(IV)/dt in this equation was calculated after the fit of a polynom of the third degree to the IV in every series by the method of least squares. As

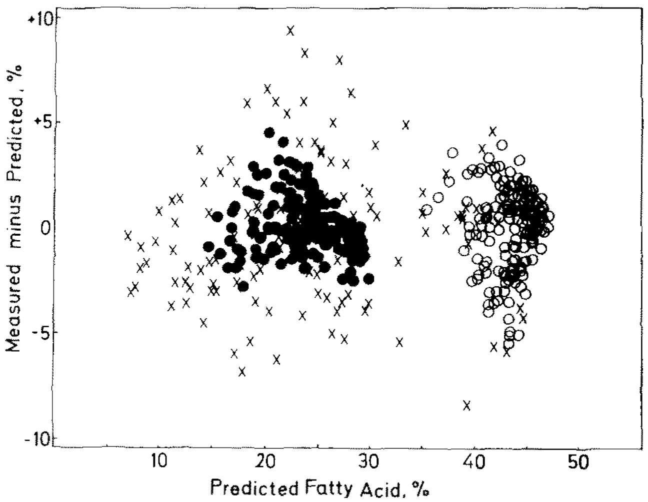

FIG. 2. Residuals vs predicted fatty acid % by wt. o = Residuals of 134 values of C(22.1); • = residuals of 122 values of C(18.1); x = residuals of 116 values of C(*trans*). All experimental values but those at the start of the hydrogenations provide the basis of the plot. Five residuals for C(*trans*) greater than 10% are not given in the plot.

also found in part 1 of this study, it was not necessary to correct the fatty acid composition for the influence of the external mass transport resistance.

Methods for Testing the Mathematical Model

Because the experimental data are serial correlated in time, a correct statistical analysis may be very troublesome (12) and was not carried out. Therefore, the estimated standard deviation between predicted and experimental wt fractions of fatty acids in glycerides was the only measure of the fit. The adequacy of the mathematical models was tested by a residual analysis, i.e., the differences between experimental and predicted wt fractions versus the predicted values were plotted.

RESULTS AND DISCUSSION

Results of Experiments

The results are not reported in detail here because they are extensive, but can be obtained from the authors. Some comments on the results are in order. In Figure 1, the influence of temperature is given at constant pressure p^o = 1.2 atm. As can be seen from Figure 1, the hydrogenation rate increases with increasing temperature to 200 C. At 220 C, a lower reaction rate was obtained than at 200 and 180 C. The decrease in the reaction rate at high temperatures, which indicates a sharp decrease of reactant adsorption, is a well known property of hydrogenations in gas phase (13, 14) and liquid phase (15), and also has been reported in fat hydrogenations (16). This property considerably complicates the mathematical model, and, therefore, the data above 200 C were not included in the calculations.

Results of Mathematical Treatment

Before a discussion concerning the estimated parameters of the rate equations is presented, it should be pointed out that this type of rate equation represents a rough simplification of the chemistry, and merely provides a convenient way of numerically reproducing the observed behavior of the process. Despite these limitations, the mathematical model provides a good basis for process calculations. It may also be a good model to use when a simplified explanation of the influence of different variables on the chemistry of the process is required.

The results of fitting the mathematical model to the experimental data are given in Tables I, II, and III and

Figure 2. The reaction order α_{ij} with respect to the fatty acid in glycerides was found to be very close to unity, so the calculations were carried out with $\alpha_{ij} = 1.00$.

The estimated values of the other parameters are based on 498 data values of the C-18 acids, 312 data values of the C-20 and the C-22 acids, and 330 data values of the C-*trans* acids. The best fit of the rate equations with a standard deviation of $s_1 = 1.95$ % by wt of fatty acid in glycerides was found with the parameter values given in Tables I, II, and III for the C-18 acids. The standard deviation refers to the difference between predicted and experimental % by wt of fatty acid in glycerides. The corresponding standard deviations of the C-20 and C-22 acids were $s_2 = 0.78\%$ for both types of acids. The standard deviation of the *trans-cis* reactions was as high as $s_{tc} = 2.88\%$. The values of s_1 and s_2 may be acceptable, whereas, the value of s_{tc} indicates that the proposed mathematical model of the *trans-cis* reactions is not so good.

The reaction order β_{ij} with respect to the concentration of hydrogen is given in Table I. All the values are less than unity. Moreover, all reaction orders are temperature dependent, and quite different values are found for the various fatty acids. Both the trend and the fractional order in hydrogen are suggestive of a Langmuir type of adsorption behavior and are well known properties of liquid phase hydrogenations. It is obvious from the β values that the net formation of C(18.2) is practically independent of the hydrogen pressure, whereas, the net formation of C(18.1) is favored by low hydrogen pressure. It should be pointed out that the rate constants and the reaction orders of the C-18 acids may not be equal to those found for the same acids in cottonseed oil or soybean oil, because the high content of erucic acid C(22.1) in rapeseed oil glycerides influences the reaction condition on the surface of the catalyst. A comparison of the reaction orders $\beta_{22.1}$ and $\beta_{18.j}$ shows that high hydrogen pressure will favor the hydrogenation of erucic acid over the hydrogenation of C-18 acids. This tendency is more pronounced at low temperatures than at high ones. The fatty acids C(18.1) deviate somewhat from this general trend, as is discussed below.

The net formation of *trans* isomers is favored by low pressure, especially at high temperature. With reference to the influence of the hydrogen pressure, the net formation of *trans* isomers proceeds in a parallel manner to the net formation of C(18.1) at high temperature. This similarity is clear when the reaction orders and the differences $\beta_{18.1} - \beta_{18.2}$ and $\beta_{trans} - \beta_{cis}$ are compared, and may indicate that a major component of the *trans* isomers is elaidic acid at high temperature. The differences between the reaction order in hydrogen for different fatty acids are difficult to understand from a mechanistic point of view. First, with regard to the difference between $\beta_{18.1}$ and $\beta_{18.2}$, it is well known that the selectivity or the net formation of C(18.1) from C(18.2) is greatly dependent on the hydrogen concentration in the oil. This influence of the hydrogen concentration can be evaluated only as various exponent values in a power type rate equation for the two reactions. The different influence of the hydrogen concentration may be explained by assuming that a hydrogen atom is included in the rate determining step of the hydrogenation of C(18.2) and a hydrogen molecule in the hydrogenation of C(18.1) (6). In accordance with this theory, the difference between $\beta_{18.1}$ and $\beta_{18.2}$ was found to be ca. 0.5 in hydrogenation of cottonseed oil (8). The competitive adsorption of fatty acids and hydrogen on the catalyst, and the influence of a slow pore transport influence the reaction rate of C(18.2) and C(18.1) to various degrees at low and high hydrogen concentrations, which results in different values of the apparent reaction orders in hydrogen (8). In hydrogenation of rapeseed oil, the difference $\beta_{18.1} - \beta_{18.2}$ is less than 0.5, which may be due to the great excess of C(22.1). The difference found between $\beta_{18.1}$, $\beta_{20.1}$ and $\beta_{22.1}$ is more difficult to understand and requires further study.

TABLE I

Reaction Order β_{ij} at Catalyst Loading 0.05% Nickel

Temperature	β_{ij}						
(C)	i.j 18.3	18.2	18.1	20.1	22.1	Cis	Trans
140	0.19	0.25	0.24	0.38	0.46	0.28	0.44
160	0.22	0.27	0.34	0.37	0.48	0.27	0.46
180	0.25	0.28	0.44	0.36	0.51	0.26	0.49
200	0.28	0.29	0.54	0.35	0.53	0.25	0.51

TABLE II

Rate Constant k_{ij} at Catalyst Loading 0.05% Nickel

Temperature	$k_{ij} \times 10^2$						
(C)	i.j 18.3	18.2	18.1	20.1	22.1	Cis	Trans
140	4.30	3.14	0.60	0.43	0.86	0.94	2.41
160	9.73	7.78	1.59	0.71	1.57	1.85	4.91
180	20.7	17.0	4.00	1.10	2.91	3.41	10.0
200	41.7	34.8	9.62	1.65	4.89	5.95	18.4

The units of the rate constant are sec^{-1} (mol hydrogen/1)$^{-\beta ij}$ (g nickel/100 g slurry)$^{-1}$.

TABLE III

Activation Energy E_{ij} at Catalyst Loading 0.05% Nickel

	E_{ij} kcal/mol						
i.j	18.3	18.2	18.1	20.1	22.1	Cis	Trans
	14.5	15.5	17.8	8.8	11.3	11.9	13.2

The rate constant k_{ij} is given in Table II. The constant values are calculated from the apparent rate constant $k_{ij}(K_H)^{\beta ij}$ with $K_H = 0.0203 \exp(-710/T)$ mol/l atm and the β_{ij} values from Table I inserted. The mutual order of the rate constants of C-18 acids is $k_{18.3} > k_{18.2} > k_{18.1}$. At increasing temperature, $k_{18.1}$ increases more rapidly than $k_{18.2}$, which increases more rapidly than $k_{18.3}$. The large values of k_{trans} compared to those of k_{cis} are contrary to most previous results (8), and indicate that the major part of the *trans* acids consists of C(18.2) and C(18.1), which also was concluded above in the discussion of the reaction order in hydrogen. The difference in the temperature dependence may also be clear from the different values of the activation energies given in Table III. It is clear from Table II that when fatty acids with one double bond are compared, C(18.1) is more reactive than C(22.1) at high temperatures. Due to the high content of C(22.1) in rapeseed oil, and due to the relatively high value of $\beta_{22.1}$, the hydrogenation of erucic acid is the dominating reaction at high temperatures. The fatty acid C(20.1) is the least reactive acid in these glycerides.

The activation energies, E_{ij}, are somewhat higher than those usually found for hydrogenations (15,17,18). The activation energy, $E_{18.1}$, is notably high in comparison to $E_{20.1}$ and $E_{22.1}$.

It is rather difficult to compare and discuss the present kinetic quantities in detail, because the confidence intervals of the estimated values are lacking. Instead of a statistic analysis of ordinary type, which seemed to be impossible due to the serial correlation in time of the experimental data, the adequacy of the rate equations was tested with a residual analysis given in Figure 2, where the difference between experimental and predicted values were examined. The net formation of the C(18.1) fatty acids and *trans* isomers are those most difficult to describe with mathematical models, because these wt fractions pass through maximum values during the hydrogenations. In a good residual plot, the data points should be randomly distributed along the axis of the predicted values. As seen in Figure 2, the mathematical model may be acceptable for the C(18.1) fatty acids. The largest values on the abscissa, corresponding to the maximum values in the different runs, do not have larger residuals than the other values, and neither is any drift in the residuals observed. The mathematical model for the *trans* isomers is not equally good. The large residuals may be explained in part because the analytical method for the determinations of *trans* isomers has lower precision than the GLC method for the determination of the fatty acid. Consequently, the confidence intervals of the parameters in the mathematical model for *trans* isomers are large, and the conclusions referring to the influence of the *trans* isomers given above must be valued with this in mind.

The mathematical model for C(22.1) and C(20.1) hydrogenation is assumed to fit more easily the experimental data and, as seen in Figure 2, the residuals of the C(22.1) acid are relatively small.

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