Technical

Nickel-Catalyzed Hydrogenation of Soybean Oil:

I. Kinetic, Equilibrium and Mass Transfer Determinations

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ABSTRACT

The kinetic and equilibrium constants were determined for the hydrogenation of soybean oil on a commercial nickel catalyst in a 300-ml Parr batch reactor. These constants were used to calculate the hydrogen gas absorption coefficients by coupling mass transfer with reaction rate based on a Langmuir Hinshelwood model. The activation energy for the rate-determining step was 23 kcal/g mol whereas the adsorption energy for hydrogen was -12.5 kcal/g mol. The gas absorption coefficients varied between 0.3 to 0.7 min^{-1} as the temperature ranged between 140-180 C.

INTRODUCTION

In a previous publication, we postulated a Langmuir-Hinshelwood rate expression for the conversion of linoleic acid to oleic and stearic acids based on a surface reaction model and two types of sites for hydrogen and the triglycerides. Equation I was found to correlate the kinetic data for the hydrogenation of palm oil and groundnut oil on a commercial nickel catalyst (1,2).

$$r = \frac{mkK_H K_L C_L C_{H_2}}{(1+K_L C_L+K_O C_O+K_S C_S)(1+\sqrt{K_H C_{H_2}})^2} \qquad [I]$$

Substitution of the assumption $K_L >> K_o, K_s, 1$ (i.e., linoleic acid is more strongly adsorbed than oleic and stearic acids) yields Equation II:

$$r = \frac{m\kappa K_H C_{H_2}}{(1+\sqrt{K_H C_{H_2}})^2} \qquad [II]$$

From Equation II, a plot of $1/r^{1/2}$ against $1/C^{1/2}{}_{H_2}$ should then yield a straight line whose intercept and slope are $1/\kappa^{1/2}$ and $1/(\kappa K_H)^{1/2}$, respectively. Thus, the kinetic constant, κ, and the equilibrium constant, K_H, are determined by measuring the global reaction rate, $r = \frac{d(IV)}{dt}$, as functions of hydrogen pressure. Equation II was found to correlate the hydrogenation of groundnut oil with an activation energy of 24 kcal/gmol and the equilibrium adsorption heat of -32 kcal/gmol for hydrogen. For the case cited, the plots of IV vs time were linear, thus permitting the use of a rate of hydrogenation that was applicable for a given set of process conditions.

A kinetic experiment can thus be performed to determine the kinetic and equilibrium constants. These constants can be used in a general expression relating mass transfer coefficients in the following manner.

By a consideration of the following mass transfer processes, i.e., absorption of hydrogen, transfer of hydrogen to the external particle surface, pore diffusion and reaction as given by Equation II, the following relationship has been derived between the rate of reaction and the mass transfer resistances $1/\kappa_b a_b$ and $1/\kappa_c a_c$ (2,3).

$$r = \frac{\dfrac{C_g}{H} - \dfrac{1}{K_H\left\{\left(\dfrac{\kappa m(IV)_o}{r}\right)^{1/2} - 1\right\}^2}}{\dfrac{1}{\kappa_b a_b} + \dfrac{1}{\kappa_c a_c}} \qquad [III]$$

Thus, $\kappa_b a_b$ can be calculated by estimating $\kappa_c a_c$ from known relations (4), using κ and K_H from kinetic experiments and the rate from mass transfer experiments. Furthermore, if $\left(\frac{\kappa m(IV)_o}{r}\right)^{1/2} >> 1$, Equation III will reduce to Equation IV:

$$\frac{(C_g/H)}{r} = \left\{\frac{1}{\kappa_b a_b} + \frac{1}{\kappa_c a_c}\right\} + \frac{1}{m}\frac{1}{K_H \kappa (IV)_o} \qquad [IV]$$

A plot of C_g/rH against $1/m$ will yield a slope of $\frac{1}{K_H \kappa}$ and an intercept of $\left(\frac{1}{\kappa_b a_b} + \frac{1}{\kappa_c a_c}\right)$. For this case, only mass transfer experiments are required for the determination of the sum of the mass transfer resistances. However, the kinetic and equilibrium constants occur as a product and the kinetic constant cannot be isolated by mass transfer experiments alone.

The procedure just described has been used in this investigation to determine the kinetic, equilibrium and mass transfer constants for the nickel-catalyzed hydrogenation of soybean oil. Selectivity determinations based on the more general kinetic expression in Equation I is the subject of a second paper in this series.

EXPERIMENTAL

Apparatus

The hydrogenation of soybean oil was done in a batch Parr 300-ml pressure reactor. The Parr reactor contained a 4-blade turbine impeller which was driven by a variable speed motor with speeds up to 1,725 rpm. This reactor has been used in our two previously reported investigations on oil hydrogenation (1,2).

Materials

Commercially available refined soybean oil was used in this investigation. High purity cylinder hydrogen was used for the hydrogenation. A commercial nickel catalyst, Girdler

G-III nickel-subsulfide on alumina suspended in a protective medium, was used in this investigation. The catalyst was ground to powder form before use.

Procedure

The procedure for monitoring the progress of the hydrogenation reaction has been described previously (1). The refractive indices at 50 C of soybean oil hydrogenated to varying degrees of saturation were calibrated against iodine values determined by the Wijs solution method. This calibration was subsequently used for the determination of the iodine value of other hydrogenated oils. A least squares fit of the relationship between the refractive index at 50 C and the iodine value for soybean oil is given by:

$$n_D^{50} = 1.3901 + 0.0007329\,(\mathrm{IV}),\ \text{where}$$

n_D^{50} = refractive index at 50 C with sodium lamp

IV = iodine value

A total of 150 ml of soybean oil was used in the 300-ml Parr reactor with varying weights of catalyst.

The GLC analysis (1) gave the following percentage composition for the soybean oil used in this investigation: 16:0(11.6), 18:0(6.9), 18:1(29.1), 18:2(50.1) and 18:3 (2.4).

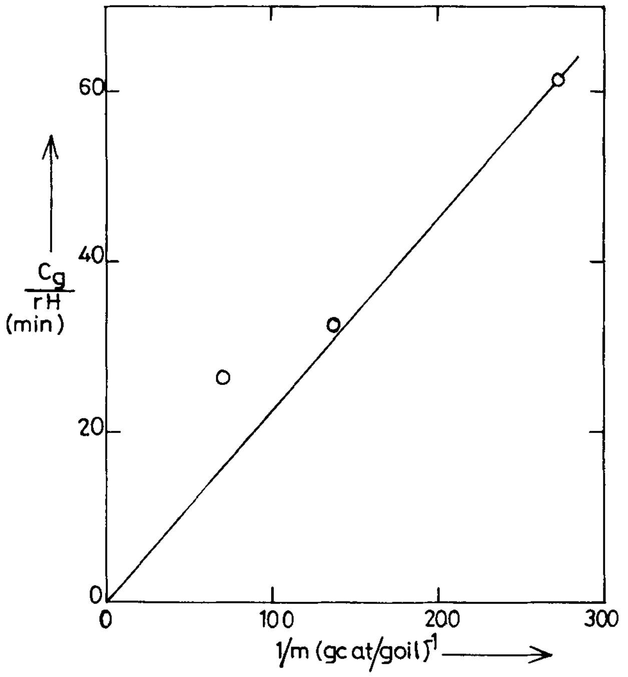

FIG. 1. Plot of $\frac{C_g}{Hr}$ vs 1/m at 160 C, 80 psig and 1,725 rpm.

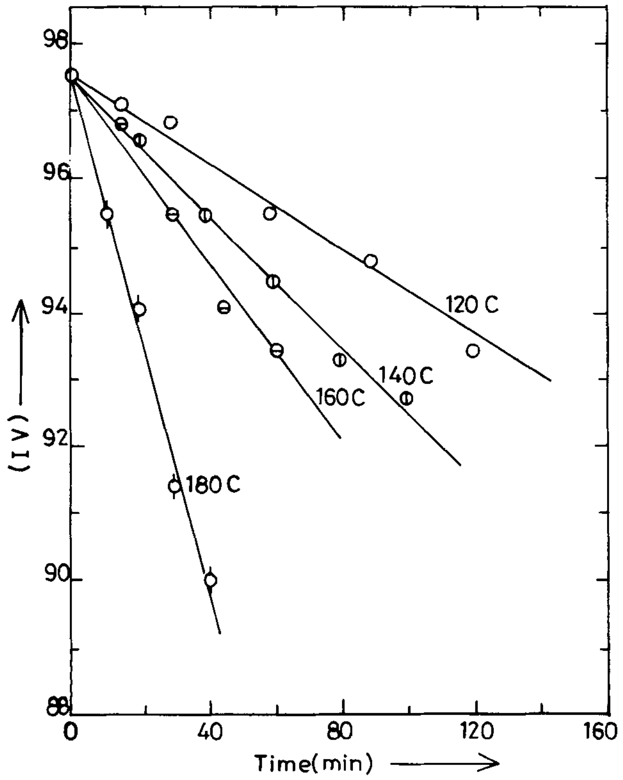

FIG. 2. IV vs time at 40 psig and several temperatures at a catalyst loading of 0.00737 g cat/g oil.

RESULTS

One of the two schemes outlined earlier (see Introduction) for the determination of kinetic, equilibrium and mass transfer constants requires the performance of a kinetic experiment for determining the kinetic and equilibrium

TABLE I

Summary of Kinetic Data at a Catalyst Loading of 0.00737 g cat/g oil and 1,725 rpm

Temp (C)	Pressure (psig)	Rate constants (min^{-1}) From (IV) plot (κ_0)
120	40	0.0340
	60	0.0659
	80	0.0710
140	40	0.0498
	60	0.0783
	80	0.0842
160	40	0.0728
	60	0.0871
	80	0.125
180	40	0.1910
	60	0.2525
	80	0.2526

TABLE II

Summary of Mass Transfer Data at 80 psig and 490 rpm

Temp (C)	Catalyst loading (g cat/g oil)	Rate constants (min^{-1}) From (IV) plot (κ_0)
100	0.00737	0.0290
140	0.00737	0.0467
160	0.00737	0.0697
180	0.00737	0.1311
100	0.01474	0.0461
140	0.01474	0.0641
160	0.01474	0.0811
180	0.01474	0.1288
100	0.02211	0.0594
140	0.02211	0.0909
160	0.02211	0.0993
180	0.02211	0.1480

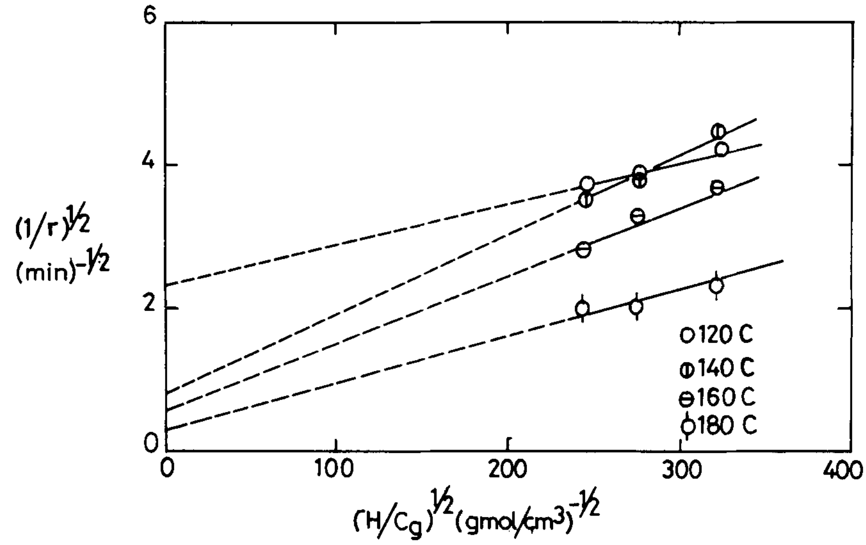

FIG. 3. Plot of $1/r^{1/2}$ vs $(H/Cg)^{1/2}$ at several temperatures for kinetic data using Equation II.

constants. Twelve hydrogenation runs were made for the kinetic experiment at pressures from 40 to 80 psig, temperatures from 100 to 180 C and at a maximum agitation rate of 1,725 rpm. Furthermore, the independence of the kinetic data from mass transfer incursions was verified by varying the catalyst loading from 0.00369 to 0.01414 g cat/g oil at 1,725 rpm. As shown in Figure 1, a plot of C_g/Hr vs 1/m is linear and passed through the origin for data at low catalyst loadings, confirming the absence of mass transfer effects (2,3). At high catalyst loading, the data deviates from a linear behavior largely because of agglomeration of catalyst particles.

Typical plots of the iodine value (IV) against time are shown in Figure 2 at 40 psig, 120 to 180 C, 1,725 rpm and a catalyst loading of 0.00737 g cat/g oil. Table I shows the summary of experimental data for the kinetic runs. A linear IV plot is desirable because the rate so obtained is representative of the hydrogenation process for a given set of process variables. We have therefore used the rate of hydrogenation from the IV plots in subsequent calculations.

Table II shows the summary of experimental data for the mass transfer runs performed at a constant pressure of 80 psig, 100 to 180 C, catalyst loadings from 0.00737 to 0.02211 g cat/g oil and a constant stirrer speed of 490 rpm. The plots of IV vs time were linear and these were again used for the rates of hydrogenation.

The range of the iodine value change obtained during this investigation was narrow. From an initial value of 97, further hydrogenation did not occur beyond iodine values of 89 and 86 for the kinetic and mass transfer experiments, respectively. GLC analysis of the hydrogenated oil after esterification indicated, for the kinetic experiments, that linoleic acid was hydrogenated to oleic and stearic acids. No further hydrogenation of oleic acid occurred. It can thus be concluded that the hydrogenation stopped at the conditions of this investigation after the exhaustion of the linoleic acid content of the soybean oil.

DISCUSSION

Kinetic and Equilibrium Constants

The kinetic and equilibrium constants were determined by the use of Equation II. The concentration of hydrogen at the catalyst surface, C_{H_2}, is given by the hydrogen concentration at the gas-liquid interface ($C_{H_2} = C_g/H$). This is because mass transfer effects are negligible in the kinetic experiments (3). Figure 3 shows plots of $1/r^{1/2}$ against $(H/C_g)^{1/2}$ at various reaction temperatures. These plots are linear as predicted by Equation II. Values of κ and K_H obtained from the intercepts and slopes of these plots at various temperatures are listed in Table III. Arrhenius plots for κ and K_H are shown in Figure 4. Least squares fit of

TABLE III

Temperature Dependence of κ and K_H

Temp (C)	κ (min^{-1})	K_H (cm^3/gmol)
120	0.26	74193
140	0.97	10309
160	4.94	2065
180	11.11	2130

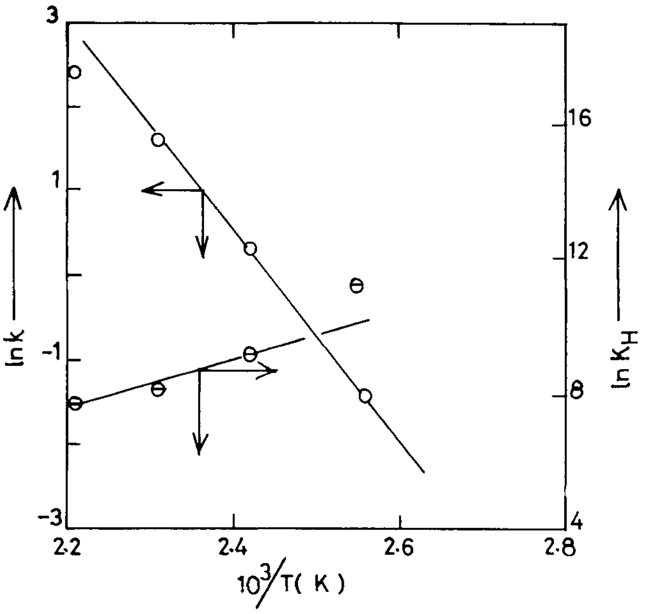

FIG. 4. Arrhenius plot for κ and K_H from Equation II for kinetic data.

the data yielded an activation energy of 23 kcal/gmol and the adsorption equilibrium energy for hydrogen of -12.5 kcal/gmol. The activation energy of 23 kcal/gmol for the hydrogenation of soybean oil compares favorably with the value of 24 kcal/gmol obtained in a previous investigation for the hydrogenation of groundnut oil on the same commercial nickel catalyst. However, the adsorption equilibrium energy of -12.5 kcal/gmol obtained from soybean oil is lower than the value of -32 kcal/gmol obtained previously for groundnut oil (2). The low adsorption energy suggests weaker interaction of hydrogen with the sulfided nickel surface. The explanation for the difference in hydrogen adsorption on the same catalyst for soybean and groundnut oil eludes us, as the presence of linolenic components in soybean oil should not exclude the strong chemisorption of hydrogen. Although no literature value for the adsorption energy ($-Q_H$) is available for comparison, a higher limit of the energy can be estimated from Equation V:

$$(-Q_H) = E(H\text{-}H) - 2\,E(H\text{-}S) \qquad [V]$$

E(H-H) is the dissociation energy of the hydrogen molecule (103 kcal/gmol)^5 and E(H-S) is the energy of the surface hydrogen-sulfur bond. The gas phase bond energy of 74 kcal/gmol was used for E(H-S) (5). The calculated value of $Q_H = -45$ cal/gmol is high because no account is taken of the energy required for breaking surface nickel-sulfur bonds (6). This calculation would suggest a stronger hydrogen chemisorption than was obtained for soybean oil in this investigation.

MASS TRANSFER COEFFICIENTS

As detailed in the Introduction, Equation IV is obtained when $\left(\frac{\kappa m(IV)_o}{r}\right)^{1/2} >> 1$. Equation IV can now be compared to the well known relationship in Equation VI:

$$\frac{(C_g/H)}{r} = \frac{1}{\kappa_b a_b} + \frac{1}{m}\left(\frac{1}{\kappa_c a_c} + \frac{1}{\kappa}\right) \qquad [VI]$$

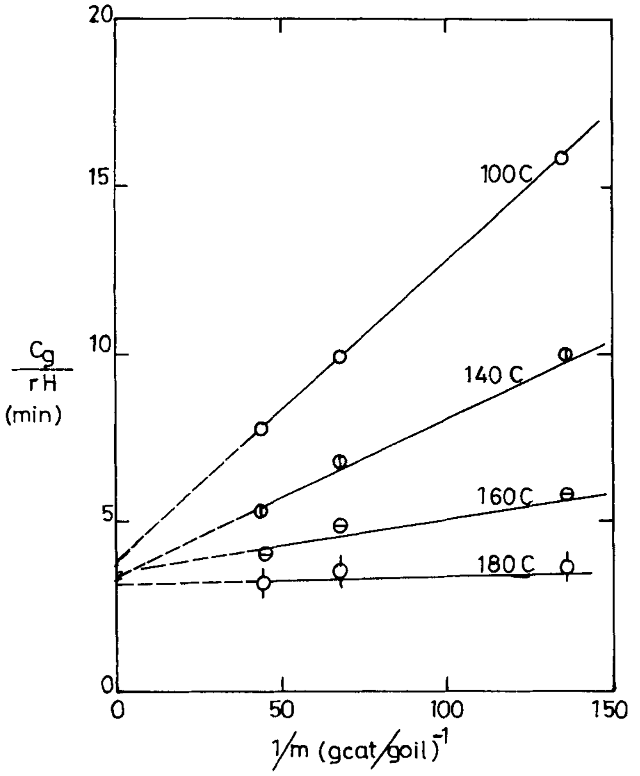

FIG. 5. Plot of $\frac{C_g}{rH}$ vs 1/m at 80 psig, 490 rpm and several temperatures for mass transfer data using Equation IV.

Equation VI was derived for mass transfer in slurry reactors in which the catalyst is suspended and for which the surface reaction is first order. A plot of $\frac{(C_g/H)}{r}$ vs 1/m should yield $1/\kappa_b a_b$ as intercept and $\left\{1/\kappa_c a_c + \frac{1}{\kappa}\right\}$ as the slope. This equation has been used extensively for the calculation of the gas absorption resistance, $1/\kappa_b a_b$, and the reaction resistance, $1/\kappa$, when $\kappa_c a_c$ can be estimated. We have shown previously that this equation might not be useful in certain cases (2). The more general relationship given by Equation IV yields a slope of $\frac{1}{K_H \kappa (IV)_o}$ and an intercept of $\left(\frac{1}{\kappa_b a_b} + \frac{1}{\kappa_c a_c}\right)$.

Figure 5 shows a plot of $\frac{(C_g/H)}{r}$ against 1/m for the four temperatures studied in this investigation. All the plots are linear and values of the slope and intercept determined by least squares analysis are shown in Table IV. An Arrhenius plot for κK_H is shown in Figure 6. Least squares fit of the

TABLE IV

Temperature Dependence of Constants from Equation IV

Temp (C)	$\frac{1}{\kappa_b a_b} + \frac{1}{\kappa_c a_c}$ (min)	κK_H (cm^3/gmol/min)	$\kappa_c a_c$ (calcd) (min^{-1})	$\kappa_b a_b$ (min^{-1})
100	3.8	11.3	3.79	0.28
140	3.3	21.2	7.33	0.31
160	3.8	69.2	9.82	0.27
180	3.0	226.2	12.65	0.34

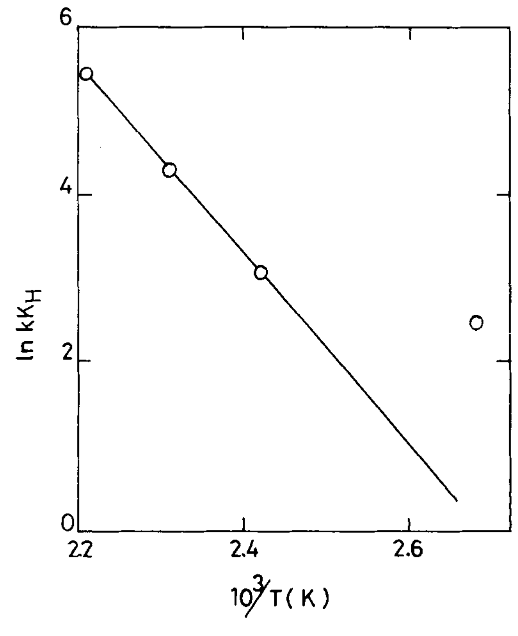

FIG. 6. Arrhenius plot for κK_H from Equation IV for mass transfer data.

TABLE V

Mass Transfer Coefficients from Equation III

Temp (C)	Catalyst loading (g cat/g oil)	$\frac{1}{\kappa_b a_b} + \frac{1}{\kappa_c a_c}$	$\left(\frac{\kappa_m(IV)_o}{r}\right)^{1/2}$	$\kappa_b a_b$ (min^{-1})
100	0.00737	--	1.1	---
140	0.00737	3.4	3.9	0.3
160	0.00737	1.6	7.2	0.63
180	0.00737	1.4	7.8	0.70
100	0.01474	---	1.2	---
140	0.01474	4.0	4.6	0.25
160	0.01474	3.4	9.4	0.29
180	0.01474	2.7	11.2	0.38
100	0.02211	---	1.2	--
140	0.02211	3.1	4.8	0.33
160	0.02211	3.8	10.4	0.26
180	0.02211	2.5	12.8	0.40

data resulted in a composited activation energy of 21 kcal/gmol. Furthermore, the fact that the composited activation energy obtained from the mass transfer experiment is of the same order of magnitude as the activation energy obtained from the kinetic experiment is a confirmation of the low adsorption energy of hydrogen on the nickel-subsulfide catalyst surface.

In order to validate the above argument, we must show that the assumption $\left(\frac{\kappa m(IV)_o}{r}\right)^{1/2} >> 1$ is valid for our experimental data. We can now use the more general expression of Equation III to estimate $\left(\frac{\kappa m(IV)_o}{r}\right)^{1/2}$ and then calculate the sum of the absorption and catalyst surface resistances $\left(\frac{1}{\kappa_b a_b} + \frac{1}{\kappa_c a_c}\right)$. Values of $\left(\frac{\kappa m(IV)_o}{r}\right)^{1/2}$ are shown in Table V for various temperatures and at three catalyst loadings. Except for the values at 100 C where the value of $\left(\frac{\kappa m(IV)_o}{r}\right)^{1/2}$ is of the order of unity, the values generally ranged between 4 and 13. We can now compare values of $\left\{\frac{1}{\kappa_b a_b} + \frac{1}{\kappa \kappa_c a_c}\right\}$ determined from Equations III and V. These values are given in Tables IV and V and these two values are in fair agreement. It can thus be concluded that the simplified relationship given in Equation IV can be used to correlate mass transfer data for hydrogenation in slurry reactors.

GAS ABSORPTION COEFFICIENT, $\kappa_b a_b$

Values of $\kappa_b a_b$ can be determined if $\kappa_c a_c$ can be estimated. The external mass transfer coefficient, κ_c, and the external catalyst area, a_c, were calculated by the use of the relationships (4):

$$\kappa_c = 2D_{H_2/oil}/d_p \text{ and } a_c = 6m/\rho_p d_p$$

Diffusion coefficients for hydrogen in cottonseed oil were used in these calculations. Values of $\kappa_b a_b$ determined in this manner by using Equations IV and III are shown in Tables IV and V, respectively. These values varied between 0.3 and 0.7 (min^{-1}) as the temperature increased from 140 to 180 C. The use of κ and K_H from the kinetic experiments to evaluate $\kappa_b a_b$ resulted in negative values for the right-hand side of Equation III at 100 C. The reason for this is obscure, but may be due to different kinetics prevalent at lower temperatures.

NOMENCLATURE

a_b, gas liquid interfacial area/unit vol of oil (cm^{-1}); a_c, catalyst surface area/unit mass of oil (cm^2/g oil); C, concentration (g mol/cm^3); d_p, catalyst particle diameter (cm); $D_{H_2/oil}$, diffusion coefficient of hydrogen in oil (cm^2/s); IV, iodine value; $(IV)_o$, initial iodine value; K, adsorption equilibrium constant; κ, rate constant (min^{-1}); κ_c, mass transfer coefficient to catalyst particle (g oil/cm^2/min); κ_b, mass transfer coefficient to liquid phase (cm/min); L, linoleic acid; m, catalyst charge (g cat/g oil); O, oleic acid; r_s, chemical reaction rate (g mol/cm^3/min) stearic acid.

Subscripts; H, hydrogen atom; H_2, hydrogen molecule. Greek letters: ρ_p, particle density.

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