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ORIGINAL PAPER

Hydrogenation of Edible Oils: a Model Involving Competitive Adsorption of Reactants

Haiyi Xiao · Shashi B. Lalvani

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Abstract A model involving competitive adsorption of reactants for hydrogenation of fatty acids was developed and analyzed. The model was established based on data obtained from catalytic transfer hydrogenation of peanut, corn, and soybean oils and soybean lecithin with aqueous sodium formate solution as the hydrogen donor and palladium on carbon as the catalyst. The predicted values based on the model agreed well with the experimental data as indicated by the r^2 and F test values. The rate of formate consumption, which decreased with time and the initial amount of formic acid versus the iodine value, was explained with regards to the mathematical model developed. Adsorption of reactants on the catalyst surface followed by a chemical reaction including participation of the fatty acid, formate and water were considered in this model.

Keywords Catalysis · Peanut · Corn · Soybean oil · Soybean lecithin · Formate · Iodine value · Hydrogenation · Kinetics · Mathematical model

List of Symbols

A	Linolenic acid
B	Linoleic acid
C	Oleic acid
D	Stearic acid
P	Formate
W	Water
Q	Bicarbonate ion
K	Rate constant
t	Time
X_i	Various species
X_{iS}	Species X_i occupied on active sites
S_v	The number of active sites on the catalyst
S_t	The total number of sites

Subscripts

1	Linolenic
2	Linoleic
3	Oleic
i	Ratio of forward to backward rate constant
ai	Adsorption
di	Desorption
o	Initial

H. Xiao · S. B. Lalvani (✉)
Department of Paper and Chemical Engineering,
Miami University, Oxford, OH 45056, USA
e-mail: lalvansb@muohio.edu

Introduction

A number of investigations have focused on various reaction chemistries that result in lowering heart disease caused by *trans* fatty acids. In one such process, Smidovnik et al. [1] have shown that when soybean oil is reacted in the presence of formic acid (and or formate) and water adsorbed on palladium catalyst, hydrogen from the formate ion and water is transferred to the oil. A significant advantage of this process is that hydrogenation can be carried out at low temperatures (80 °C and above) and atmospheric pressure. A typical reaction mixture contains 2.8 M formate ion with an oil/water ratio of 1:2 by weight. The reaction mechanism involves adsorption of formate, oil and water on the catalyst surface followed by hydrogenation.

Smidnovik et al. [2] employed the first-order irreversible reaction mechanism. Mondal and Lalvani [3] employed a second-order model to study the reaction kinetics. Blanermer et al. [4], Summers et al. [5], Klemn and Klemn [6] have considered more complex and second-order reaction mechanisms. None of these investigations, however, have considered adsorption of reactants on the catalyst surface followed by a chemical reaction.

Model Development

In the model presented below, the overall reaction mechanism involves hydrogenation of linolenic acid (*A*) to linoleic (*B*), which in turn is converted to oleic acid (*C*) via a series of reaction steps. If the overall reaction goes to completion, then the final product is stearic acid (*D*) as shown in Eq. 1. The actual reaction involves participation of the fatty acid, formate (P) and water (W), resulting in products that contain a host of fatty acids and the bicarbonate ion (Q) as indicated by Eq. 1a–c.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \tag{1}$$

$$A + P + W \xrightarrow{k_1} B + Q \tag{1a}$$

$$B + P + W \xrightarrow{k_2} C + Q \tag{1b}$$

$$C + P + W \xrightarrow{k_3} D + Q \tag{1c}$$

The first step during the reaction involves adsorption of various species (X_i) on the surface of the catalyst as shown by the following equation.

$$X_i \overset{k_{\mathrm{ai}}}{\underset{k_{\mathrm{di}}}{\Leftrightarrow}} [X_iS] \tag{2}$$

where $[X_iS]$ represents the complex formed due to occupation of active sites by the species X_i. K_{ai} and K_{di} are the adsorption and desorption rate constants. The overall rate of $[X_iS]$ generation is given by

$$\frac{d[X_iS]}{dt} = k_{\mathrm{ai}}X_iS_v - k_{\mathrm{di}}[X_iS] \tag{3}$$

where, S_{v} is the number of active sites present. Assuming pseudo steady-state [i.e. $\frac{d[X_iS]}{dt} = 0$] gives us

$$[X_iS] = k_iX_iS_{\mathrm{v}} \tag{4}$$

In the theory of active intermediates as explained by Fogler [7], the time lag for decomposition of the intermediates, such as $[X_{\mathrm{i}}S]$ is infinitesimally small and, therefore, the assumption regarding pseudo-steady state was reasonable in their work.

Where, k_{i} is the ratio of forward to backward rate constant in Eq. (3). The total number of sites, S_{t} is given by the sum of vacant sites and the sites occupied by various species, i.e.

$$S_{\mathrm{t}} = S_{\mathrm{v}} + \left[\sum X_iS\right] \tag{5}$$

Substitution of (4) in (5) gives us

$$S_{\mathrm{v}} = \frac{S_{\mathrm{t}}}{1 + \sum k_iX_i} \tag{6}$$

The rate expression of species *A* is given by the following:

$$\frac{dA}{dt} = -k_1[AS][PS][WS] \tag{7a}$$

Substitution of concentration of occupied sites given by Eq. (4) into the above expression yields

$$\frac{dA}{dt} = -k_1k_Ak_Pk_WAPWS_v^3 \tag{7b}$$

Similarly, from Eq. (1a–c) we obtain the following:

$$\frac{dB}{dt} = k_Pk_W(k_1k_AA - k_2k_BB)PWS_v^3 \tag{8}$$

$$\frac{dC}{dt} = k_Pk_W(k_2k_BB - k_3k_C)PWS_v^3 \tag{9}$$

$$\frac{dD}{dt} = k_3k_Ck_Pk_WCPWS_v^3 \tag{10}$$

$$\frac{dP}{dt} = \frac{dW}{dt} = -\frac{dQ}{dt} \tag{11}$$

The overall mass balance on reactants *A*, *B*, *C* and *D* (i.e. the sum of Eqs. (7b–10) is made under the assumption that the amount of hydrogen transfer to the fatty acid is minimal in relation to their total mass, which allows for the following mass conservation equation:

$$A + B + C + D = A_o + B_o + C_o + D_o \tag{12}$$

where, $A_{O,}$ $B_{O,}$ C_O and D_O represent the initial concentrations of the respective components. The use of Eq. 12 eliminates the need for one of the four differential equations (Eqs. 7b–10). The solution to the differential equations listed above involves expressing the concentration of reactants in terms of *A* and then solving the resultant differential equation. This approach is the same as described by Mondal [3]. When Eqs. (8) and (9) are divided by Eq. (7b), the following differential equations are obtained

$$\frac{dB}{dA} - \alpha\frac{B}{A} = -1 \tag{13a}$$

$$\frac{dC}{dA} - \beta\frac{C}{A} = -\alpha\frac{B}{A} \tag{13b}$$

where

$$\alpha = k_2 k_B/(k_1 k_A) \tag{14a}$$

and,

$$\beta = k_3 k_C/(k_1 k_A) \tag{14b}$$

The solution to the linear, first-order differential equation (13a) is given by

$$B = -\left(\frac{1}{1-\alpha}\right)A + C_1 A^{\alpha} \quad \alpha \neq 1 \tag{15a}$$

$$= -A \ln A + C_1 A \quad \alpha = 1 \tag{15b}$$

In the above equations, C_1 represents the constant of integration.

The solution to equation (13b) is given by

$$C = -\alpha A^{\beta} \int \left(\frac{B}{A}\right) A^{-\beta} \mathrm{d}A + C_2 A^{\beta} \tag{16}$$

Substitution of Eqs. (15) in (13b) allows for the evaluation of the concentration of component C, where C_2 is the constant of integration. Substitution of B, from Eq. (15a) and (b), results in expressions for C in terms of concentration A. The following five distinct cases cover all range of data, which are reported in Table 1.

Concentrations of species W, P and Q are determined by noting that

$$\frac{dW}{dt} = \frac{dP}{dt} = -\frac{dQ}{dt} = 3\left(\frac{dA}{dt}\right) + 2\left(\frac{dB}{dt}\right) + \left(\frac{dC}{dt}\right)$$

From the above expression, we get the following

$$W - W_o = P - P_o = -(Q - Q_o) = 3(A - A_o) + 2(B - B_o) + (C - C_o) \tag{17}$$

Since the concentrations B and C are evaluated in terms of concentration A (Table 1), the above expression allows us to express the concentrations of W, P, and Q in terms of concentration A. This also allows the evaluation of S_V from Eq. (6) in terms of the concentration A. This procedure allows for integration of Eq. (7b), which is rewritten as

$$\int_{A_o}^{A} \frac{\mathrm{d}A}{APWS_v^3} = -k_1 k_A k_P k_W t \tag{18}$$

Results and Discussion

Simulation of the kinetics of formic-assisted hydrogenation of peanut, corn and soybean oils, as well as soybean lecithin, was carried out using commercially available software (Polymath). Equations 7b through 12 along with Eq. 6 form the body of the mathematical model. Experimental data obtained from papers by Naglic et al. [8, 9] were fitted to the model to estimate the rate constants, which are listed in Table 2. Figure 1 is a typical plot of the fatty acid composition of peanut oil versus time. A visual inspection of the data shows that model predictions are in good agreement with the experimental data. Similarly, Fig. 2 is a plot of the fatty acid profile of soybean oil. Again, the fit between the experimental data and the model-generated results was good, as described below.

In order to quantify the results obtained by the model developed in this study, regression analysis was carried out. The data for linolenic, linoleic, oleic and stearic fatty acids are shown in Table 3. The average r^2 value for all data reported was 0.97. With the exception of one data point, which corresponds to the r^2 value for the stearic fatty acid of corn oil, the rest of the regression values are very good to excellent (r^2 greater than 0.935). The average r^2 value is in agreement with that reported by Mondal and Lalvani [3].

In addition to the regression analysis, F test data were obtained to estimate the goodness of fit between the experimental and the model data (Table 4). The average value of 0.87 was deemed to be very good, especially when contrasted with the corresponding number of 0.05 obtained by Mondal and Lalvani [8], whose assumption that hydrogenation kinetics can be described by invoking homogenous reaction pathways, is apparently not valid. A value of 1.0 denotes a perfect match.

Table 1 Integrated expression for concentrations of B (linoleic) and C (oleic)

	B	C
Case I $\alpha \neq 1$, $\beta \neq 1$, $\alpha \neq \beta$	$-\left(\frac{1}{1-\alpha}\right)A + C_1A^{\alpha}$	$\frac{\alpha A}{(1-\alpha)(1-\beta)} - \frac{\alpha C_1 A^{\alpha}}{(\alpha-\beta)} + C_2A^{\beta}$
Case II $\alpha \neq 1$, $\beta \neq 1$, $\alpha = \beta$	$-\left(\frac{1}{1-\alpha}\right)A + C_1A^{\alpha}$	$\frac{\alpha A}{(1-\alpha)^2} - \alpha C_1 A^{\alpha} 1\mathrm{n}\, A + C_2 A^{\alpha}$
Case III $\alpha \neq 1$, $\beta = 1$	$-\left(\frac{1}{1-\alpha}\right)A + C_1A^{\alpha}$	$\frac{\alpha}{(1-\alpha)} A\ 1\mathrm{n}\, A + \frac{\alpha C_1 A^{\alpha}}{1-\alpha} + C_2 A$
Case IV $\alpha = 1$, $\beta \neq 1$	$-A\ln A + C_1 A$	$\frac{A}{(1-\beta)^2}[(1-\beta)(\ln A - C_1) - 1] + C_2A^{\beta}$
Case V $\alpha = 1$, $\beta = 1$	$-A \ln A + C_1 A$	$-A \ln A + C_1 A + C_2 A$

C_1 and C_2 are determined from the initial conditions

W, P and Q can be expressed in terms of A (see Eq. 18)

$\alpha = k_2 k_B/(k_1 k_A)$ and $\beta = k_3 k_C/(k_1 k_A)$

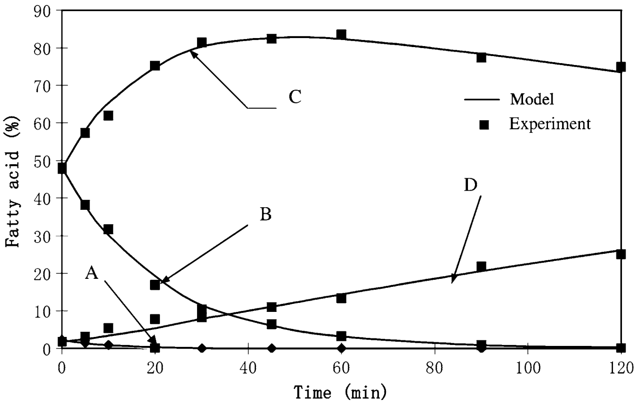

Fig. 1 Fatty profile versus time experimental data from Nalgic et al. [8] for peanut oil

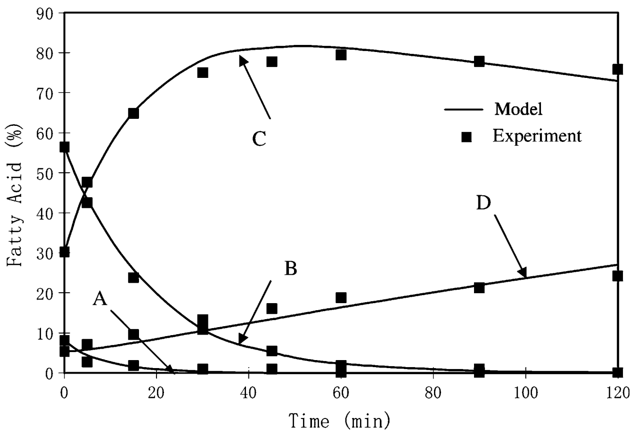

Fig. 2 Fatty profile versus time experimental data from Nalgic et al. [8] for soybean oil

Table 2 Calculated rate constants

	Peanut oil	Corn oil	Soybean oil	Soybean lecithin
K_A	0.001	0.001	0.001	0.001
K_B	0.001	0.001	0.001	0.001
K_C	0.001	0.001	0.001	0.001
K_P	0.001	0.0025	0.001	0.001
K_W	0.001	0.0003	0.001	0.001
K_1	0.07	0.5	0.09	0.027
K_2	0.038	0.18	0.05	0.016
K_3	0.0023	0.01	0.023	0.008

Table 3 Calculated regression (r^2) coefficients

	Linolenic acid	Linoleic acid	Oleic acid	Stearic acid
Peanut oil	0.978	0.997	0.988	0.983
Corn oil	0.945	0.996	0.987	0.821
Soybean oil	0.935	0.999	0.987	0.949
Soybean lecithin	0.958	0.993	0.968	0.989

Table 4 Calculated *F* test data

	Linolenic acid	Linoleic acid	Oleic acid	Stearic acid
Peanut oil	0.93	0.97	0.90	0.86
Corn oil	0.96	0.86	0.85	0.83
Soybean oil	0.82	0.98	0.91	0.72
Soybean Lecithin	0.57	0.99	0.92	0.90

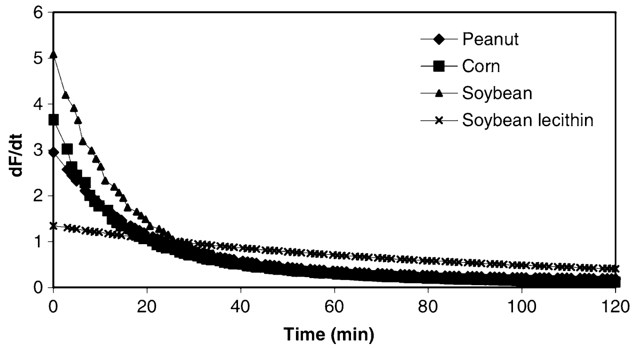

Fig. 3 The rate of formate ion consumption versus time

The rate of formate ion consumption as a function of time is shown in Fig. 3. As expected, the rate decreased with time. Contrary to what kinetic considerations dictate, the model developed by Mondal and Lalvani [10] predicted the rate of hydrogenation does not decrease monotonically with time. Significant oscillations in the rate of formate consumption with time were observed, and no simple explanation was offered by the authors to explain the results. Mondal and Lalvani [11] responded by offering the view that the formation of conjugate dienes, the higher rate of double bond migration as compared to the rate of hydrogenation of dienes in the presence of conjugated dienes, the retardation of migration of double bonds in the presence of linolenic fatty acid, and monopolization of catalyst active sites by higher-order unsaturated fatty acids could lead to the formate consumption rate oscillations. However, they presented very little evidence for this hypothesis.

Another significant result is the plot of iodine value versus the initial amount of formic acid (Fig. 4). The iodine value (IV) was computed from the fatty acid composition. The data show that IV decreases with the amount of formic acid, as would be expected, however, when the formic acid concentration exceeds 250 (arbitrary units), the IV is observed to increase. Naglic et al. [8], have shown that the hydrogenation step requires the presence of oil, formate ion as well as water on the catalyst surface. There is

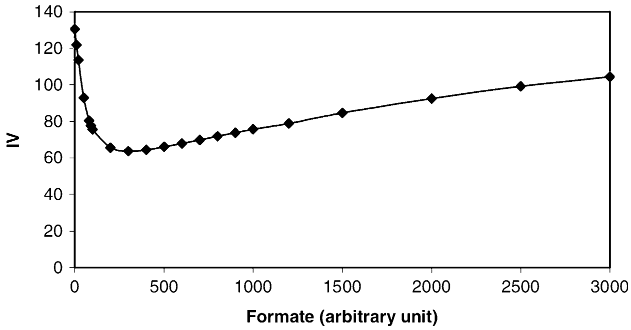

Fig. 4 Iodine value versus the initial amount of formic acid

competitive adsorption of the three reagents; the relative amount of the three species adsorbed on the surface determines the overall rate of oil hydrogenation. According to previous hydrogenation models including the one developed by Mondal and Lalvani [10], which treated hydrogenation as a homogeneous reaction, the IV of the hydrogenated oil should decrease monotonically with the formate content. This approach is at variance not only with the experimental data but also with the known mechanism of oil reduction. The model developed here is general in nature, in that it can be easily adopted to describe the reduction of fatty acids by molecular hydrogen.

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