

Modeling of Hydrogenation Kinetics from Triglyceride Compositional Data

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A mathematical model was developed to describe the reduction of soybean oil triglycerides during hydrogenation. The model was derived from reaction and transport mechanisms and formulated into a system of first-order irreversible rate expressions that included terms for temperature, hydrogen pressure, and catalyst concentration. The model parameters were estimated from experimental data, and the model was used to simulate the results of hydrogenation performed over the pressure range of 0.069–6.9 MPa. The model could be extended to include geometrical isomers formed during hydrogenation.

KEYWORDS: Hydrogenation; soybean oil; modeling; simulation; nickel catalysts; kinetics

INTRODUCTION

The ability to direct the course of a reaction by controlling reaction conditions has significant applications in the edible oil industry. Of particular interest is the role of temperature and pressure in the hydrogenation of vegetable oils. Previously, the kinetics of hydrogenation have been described in terms of the component fatty acids, for example, linolenic, linoleic, and oleic (1–5). Current analytical methods allow the determination of triglycerides directly (6, 7). Such methods have been applied to follow the hydrogenation of soybean oil (8). This is a significant development as the health aspects of triglyceride structure and function are revealed. For example, one may desire to minimize the formation of trans-fatty acids during catalytic hydrogenation. The present study examined the use of a mathematical model to interpret kinetic data and potential applications in the partial hydrogenation of soybean oil triglycerides.

MATERIALS AND METHODS

Hydrogenation Reactions. Hydrogenation reactions were performed in a 2-L stirred reactor with a commercially extracted, refined, bleached, and deodorized soybean oil using a supported Ni catalyst as described previously (8, 9).

Analytical Methods. Triglyceride compositions of reactant and product samples were determined by reverse phase high-performance liquid chromatography (RP-HPLC) following the method of Neff et al. (6) using an evaporative light scattering detector (ELSD).

Data Analysis. Triglyceride data were analyzed using the simulation software, ScoP (Simulation Resources, Inc., Berrien Springs, MI) installed on a personal computer. A set of differential equations was formulated to represent possible hydrogenation reactions of the tri-

glyceride species. Solutions were obtained by numerically integrating the equations using a fourth-order Runge–Kutta method. The principal axis method was used to estimate parameter values from experimental data.

RESULTS AND DISCUSSION

Model equations were developed from a mechanistic consideration of the physical and chemical rate processes and a material balance on the triglyceride species. The model was based on the assumption that the reduction reaction was irreversible and proportional to the concentration of the triglyceride, hydrogen, and catalyst present. The reaction rate was known to depend on the temperature and mass transfer of reactive species to the catalyst surface. The temperature dependence of the reaction rate was expressed by an Arrhenius equation, $k_i = A \exp(-E_a/RT)$, with A , the frequency factor; E_a , the activation energy; R , the gas constant; and T , the temperature. Bulk mass transfer effects were expressed through the mass transfer coefficient, for example, k_b . Heterogeneous reactions also involve the catalyst surface where reactant adsorption, diffusion, reaction, and desorption of products occur. These effects are often treated as a series of resistance terms. The experimentally measured rate constant is the result of these mechanistic processes and may be represented in reciprocal form as $K^{-1} = \sum(\alpha\kappa)^{-1}$ with the sum formed from the product of a resistance term and the corresponding area. This expression provides a physical basis for the model and is capable of describing the behavior over a wide range of conditions (10). For example, if the surface reaction is relatively slow compared to the rate of reactant transport or adsorption, then the reaction term dominates the expression and the reaction is said to be under kinetic control, whereas a fast reaction step and relatively slow mass transfer produce a mass transfer limited condition. It may be difficult to experimentally separate these effects;

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Table 1. Correlation Coefficients for Reactions at 0.34 and 3.4 MPa and 120 °C

reaction	reactants ^a	products ^a	0.34 MPa	3.4 MPa
1	LLL	LLO	0.5993	0.2603
2	LLO	OOS	0.5867	0.1923
3	OOS	OSS	0.2501	0.1959
4	OSS	SSS	0.1083	0.0062
5	LLP	LOP	0.3079	0.0755
6	LOP	OOP	-0.1809	-0.1522
7	OOP	OSP	0.2504	0.2937
8	OSP	SSP	0.0274	-0.4105

^a L, linoleic; O, oleic; S, stearic; P, palmitic.

however, the form of the equation provides a basis to interpret the effects of temperature and mass transfer on reaction rate.

The rate expression for a particular triglyceride may then be written as the sum and differences of an overall rate constant, K , triglyceride concentration, hydrogen pressure, and catalyst concentration for the reactant and product species. Further simplification is achieved by grouping the hydrogen pressure and the catalyst concentration with the rate constant. This new constant takes the form, $K' = K(P/P_0)^p(C/C_0)^c$, with P , the pressure; P_0 , a reference pressure; C , catalyst concentration; and C_0 , a reference catalyst concentration. The superscripts represent the power of the respective term, not necessarily an integer. This form allows the introduction of dimensionless pressure and catalyst concentration terms.

The material balance equations were written on the basis of the reactants and products of the triglyceride species. A partial set of these reactions is listed in **Table 1** with the corresponding correlation coefficients. For example, triolein, designated OOO following the convention (L, linoleic; O, oleic; S, stearic; and P, palmitic), may be reduced to OOS, OSS, and SSS. In the proposed reaction scheme OOO may be formed by the reduction of LLL, LLO, and LOO. The corresponding rate equation for triolein appears in eq 1.

$$(\text{OOO})' = a_1(\text{LLL}) + a_2(\text{LLO}) + a_3(\text{LOO}) - b_1(\text{OOO}) \quad (1)$$

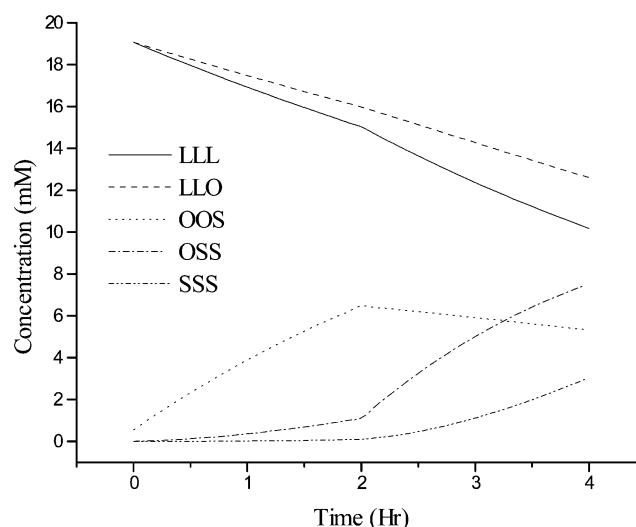
The first derivative of triolein concentration with respect to time is denoted by the prime on the left-hand side of the equation, and the corresponding formation and reduction terms appear on the right-hand side of the equation. The subscripted parameters, a_i and b_i , that appear on the right-hand side of the equation are the rate constants, K' , for the triglycerides that contribute to formation and reduction, respectively. Similar equations were written for each of the reactant triglycerides to produce a system of coupled differential equations.

This model assumed that positional isomers possess comparable chemical reactivity, although these could be treated as unique species and introduced through material balance equations. This approach could also be used for geometrical isomers. The number of reactive species and the corresponding number of differential equations in the model would increase.

The system of equations was solved numerically. An optimization algorithm was used to adjust the parameter values and compare the calculated solutions to a reference file containing experimental data. Calculations continued until a minimum value of the residuals was obtained. Statistics are summarized in **Tables 1** and **2** for model results based on the hydrogenation of a commercially refined, bleached, and deodorized soybean oil using 0.02 wt % nickel catalyst at pressures of 0.34 and 3.4 MPa at 393 K with maximum agitation (8, 9). **Table 1** presents values of the serial correlation coefficient for selected triglyc-

Table 2. Estimated Rate Constants and Standard Deviations for Reactions at 120 °C

reaction	K (h^{-1}), 0.34 MPa	SD	K (h^{-1}), 3.4 MPa	SD
1	0.119597	2.58114E-02	0.191059	1.00128E-02
2	0.204412	2.94573E-02	0.289669	1.11892E-02
3	0.153415	6.29874E-02	0.797362	5.74691E-02
4	0.110104	6.27092E-02	0.299169	2.34767E-02
5	0.636886	5.50459E-02	0.170818	6.94933E-03
6	0.543815	3.37910E-02	0.292360	1.14197E-02
7	0.334781	2.73767E-02	0.410708	2.35954E-02
8	0.212950	4.54359E-02	0.664040	6.28243E-02

**Figure 1.** Simulation of changing triglyceride distribution with increasing pressure. Reaction was initiated at 0.34 MPa, and pressure was increased to 3.4 MPa after 2 h.

eride species. These data suggest that the residuals are normally distributed. Student's t test confirmed the random distribution of the residuals with 95% probability. **Table 2** lists the fitted values of overall rate constants and the corresponding standard deviation (SD). The results of the statistical analyses provide confidence in the ability of the model to describe the experimentally observed results.

The utility of such a model is the ability to relate process variables such as pressure and temperature to the course of a hydrogenation reaction and predict the resulting triglyceride distributions. **Figure 1** shows the results of a simulation where hydrogenation is initiated at a pressure of 0.34 MPa, which is increased to 3.4 MPa after 2 h. This simulation indicates how the triglyceride distributions could be directed by controlling the pressure. This would be particularly advantageous in the partial hydrogenation of soybean oil, where a product of a specific composition is sought to provide particular material properties. The model equations were developed from a mechanistic description of the physical and chemical processes. This provides a fundamental basis to relate the change in triglyceride composition to temperature, pressure, catalyst concentration, and mass transfer. The model could be extended to include the formation of geometrical isomers in a straightforward manner if provided with additional experimental data.

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