# Modeling of Reaction Rate Constants and Selectivities in Soybean Oil Hydrogenation[1]

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## ABSTRACT

A simple approach to model the rate constants and selectivities for soybean oil hydrogenation with nickel catalyst is presented. The rate constant models were constructed on the basis of Arrhenius Law and Power series. The parameters were temperature, hydrogen pressure, concentration of catalyst and agitation expressed in terms of power per unit volume of oil. The models agree with the general knowledge in hydrogenation and the data were fitted fairly well by the models.

## INTRODUCTION

Hydrogenation of vegetable oils is one of the most crucial unit operations in the fats and oils industries. The rate of hydrogenation has a significant bearing on the economics. Further, the proper control of selective hydrogenation is of major concern to the processors. Many investigations (1-3) attempted to relate the rate constant and selectivity to various parameters such as catalyst concentration, agitation, hydrogen pressure and temperature. However, all the previous work involved complicated models which are either inconvenient or impossible for plant personnel to employ. Allen et al. (4) demonstrated the relationship between selectivity, rate constant and process parameters with Response Surface Methodology. This approach made the models more accessible in plant operation. Unfortunately, Response Surface Methodology does not relate the physical significance of the process parameters to selectivity and rate constants. It is the purpose of this paper to illustrate an approach through which semiempirical models are used to relate the kinetics to process variables. The resulting models are simple and they should have some practical applications.

## CONSIDERATION OF MODELS

Rate constants are known to follow the Arrhenius equation (5). Therefore, the temperature effect on rate constant was described by an exponential form. The Arrhenius equation is defined as:

$$k = Ae^{\frac{-E_a}{RT}} \qquad [I]$$

where k = rate constant; A = frequency factor; $E_a$ = activation energy; R = gas constant; T = absolute temperature in °K.

In all the previous work (1-4), the effect of agitation was expressed in revolutions/min (rpm). The rpm is restricted to the specific system and cannot be used in scale-up; large and small agitators might be operated at the same rpm but the degree of agitations is drastically different. In this work, the power/unit volume was employed instead. The choice of power/unit volume made the parameter an intensive variable which is independent of the system.

In chemical engineering, power series are one of the most commonly used techniques in modeling (6). The effects of hydrogen pressure, catalyst concentration and power/unit volume were expressed with the first term of the power series. The complete model is illustrated as:

$$k_i = b_0\, e^{\frac{b_1}{T}}\, P^{b_2}\, C^{b_3}\, P_0{}^{b_4}, \qquad [II]$$

where $k_i$ = rate constant in $\text{min}^{-1}$, defined in Equation III:

$$\text{Linolenic} \xrightarrow{k_1} \text{Linoleic} \xrightarrow{k_2} \text{Oleic} \xrightarrow{k_3} \text{Stearic}, \qquad [III]$$

and P = hydrogen pressure in psig; C = concentration of catalyst in ppm; $P_0$ = power/unit volume in $\text{HP/ft}^3$.

The choice of Equation II assumed that interactions among T, P, C and $P_0$ exist. It is a well known fact that interactions of these four parameters do occur; therefore, the model as indicated in Equation II is justified. Another advantage of Equation II is the ease of modeling. For example, when the natural logarithm of both sides of Equation II is taken the following equation results:

$$\ell n\, k_1 = \ell n\, b_0 + \frac{b_1}{T} + b_2\, \ell n\, P + b_3\, \ell n\, C + b_4\, \ell n\, P_0 \qquad [IV]$$

The constants in Equation IV can be determined with multiple linear regression.

Since the parameters in Equation II are all intensive variables translatable between processes, scale-up or scale-down is possible when the models are used.

## EXPERIMENTS AND CALCULATIONS

A 1-L Parr medium pressure apparatus was used as the reactor. Thirty experimental runs were conducted according to a central rotating composite design. The ranges of the parameters were: T from 523-400 K, P from 47 to 6 psig, C from 2100-300 ppm and $P_0$ from 0.068-0.0002 $\text{HP/ft}^3$. Detailed experimental procedures were given in the previously published paper (7), except the amount of oil used was 200 g in this study. One small 3-blade pitch propeller of 1-in. diameter was used for agitation. The rpm of the propeller was measured and $P_0$ was calculated as follows. The power was first calculated according to the typical power equation (8). $P_0$ was obtained by dividing the calculated power input by the volume of oil. Since the equation used for power estimation assumes a nongassed system, the effect of hydrogen gas on power was calculated according to the literature (9). The calculation showed that the effect of hydrogen gas was insignificant.

## RESULTS

The rate constant models for $k_1$, $k_2$ and $k_3$ are shown in Equations V, VI and VII, respectively.

$$k_1 = 506\, e^{\frac{-5312}{T}}\, P^{0.74}\, C^{0.31}\, P_0{}^{0.40} \qquad [V]$$

$$k_2 = 177\, e^{\frac{-5828}{T}}\, P^{0.77}\, C^{0.51}\, P_0{}^{0.36} \qquad [VI]$$

$$k_3 = 0.29\, e^{\frac{-3709}{T}}\, P^{1.02}\, C^{0.19}\, P_0{}^{0.40} \qquad [VII]$$

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The analysis of variance for the above models are summarized in Table I. The residual analysis showed that neither outliers nor trends exist, indicating the models fit the data well. The predicted values of $k_1$, $k_2$ and $k_3$ are plotted against their corresponding observed values, and they are shown in Figures 1, 2 and 3, respectively.

The selectivity of linolenic or LnSR was obtained by dividing Equation V by VI:

$$\mathrm{LnSR} = \frac{k_1}{k_2} = 2.9\, e^{\frac{516}{T}}\ P^{-0.03}\, C^{-0.20}\, P_0^{0.04} \qquad \text{[VIII]}$$

Since the exponents for P and $P_0$ are extremely small, for practical purposes they can be assumed to be zero. This reduces equation VIII to IX:

$$\mathrm{LnSR} = \frac{2.9\, e^{\frac{516}{T}}}{C^{0.2}} \qquad \text{[IX]}$$

The selectivity of linoleic or SR was obtained according to the same procedure and it is depicted in Equation X:

$$\mathrm{SR} = \frac{k_2}{k_3} = \frac{610\, e^{\frac{-2119}{T}}\ C^{0.32}}{P^{0.25}} \qquad \text{[X]}$$

## DISCUSSION

### Rate Constants ($k_1$, $k_2$ and $k_3$)

Inspection of rate constant models as shown in Equations V, VI and VII indicate that $k_1$, $k_2$ and $k_3$ are affected by the process temperature, hydrogen pressure, concentration of the nickel catalyst and the power/unit volume. It is known in the industry that the increases in T, P, C and $P_0$ should cause rapid hydrogenation. However, except in the case of temperature, there has not been any model presented in which a quantitative relationship between reaction rates and P, C, $P_0$ were considered. The rate equations V, VI and VII provide guidance to processors who wish to increase their rate of hydrogenation.

In hydrogenation, the reactions can be either mass transfer limited or kinetic controlled. Although mass transfer limiting can be overcome by intensive agitation (10), in commercial hydrogenation, mass transfer is usually the rate controlling step. Our rate constant models are functions of $P_0$, which means that consideration of mass transfer controlling is taken into account. It can be visualized that at high values of $P_0$ and P where hydrogen transfer is at its maximum, the reaction rates are dominated by their kinetics. On the other hand, mass transfer controls the rate of hydrogenation when low hydrogen pressure and low agitation are imposed upon the process. Notice the parameter of $P_0$ and P are both in exponential form, which implies that the effects of $P_0$ and P are very drastic at their low values but the effect will be leveled off when mass transfer is no longer controlling. The choice of the exponential forms for $P_0$ and P are not only for the ease of modeling as discussed earlier, but have significant physical meaning as well.

**TABLE I**

**Analysis of Variance of $k_1$, $k_2$ and $k_3$ Models**

| Rate constant | Parameter | Significant (%) | R^a |
|---|---|---|---|
| $k_1$ | T | 99.99 | 0.92 |
| | P | 99.85 | |
| | C | 89.98 | |
| | $P_0$ | 99.99 | |
| $k_2$ | T | 99.99 | 0.94 |
| | P | 99.97 | |
| | C | 99.55 | |
| | $P_0$ | 99.99 | |
| $k_3$ | T | 99.99 | 0.95 |
| | P | 99.99 | |
| | C | 87.35 | |
| | $P_0$ | 99.99 | |

[a] Correlation coefficient.

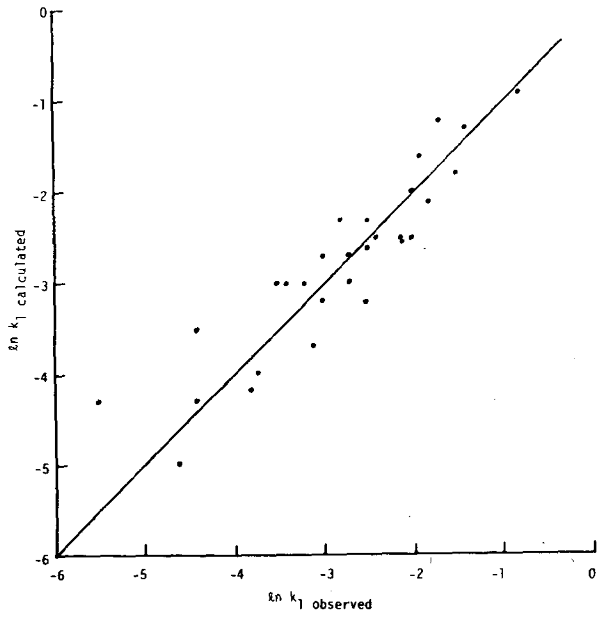

**FIG. 1. Calculated values vs observed values of $k_1$.**

Calderbank (11) reported that mass transfer is proportional to the 0.4 power of $P_0$. It can be seen from Equations V, VI and VII that the exponents of $P_0$ for $k_1$, $k_2$ and $k_3$ are 0.4, 0.36 and 0.4, respectively, which agree well with the literature.

### Selectivity Ratios (SR and LnSR)

The selectivity model illustrated in Equation X suggests that increases in temperature and concentration of catalyst should enhance the selectivity. On the contrary, the selec-

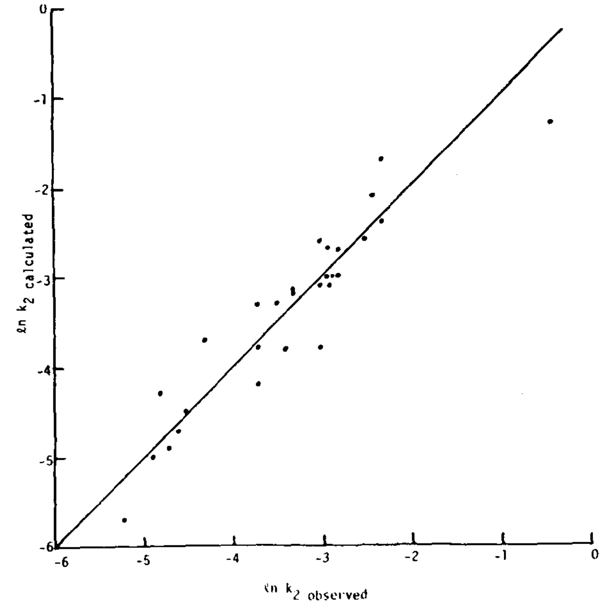

**FIG. 2. Calculated values vs observed values of $k_2$.**

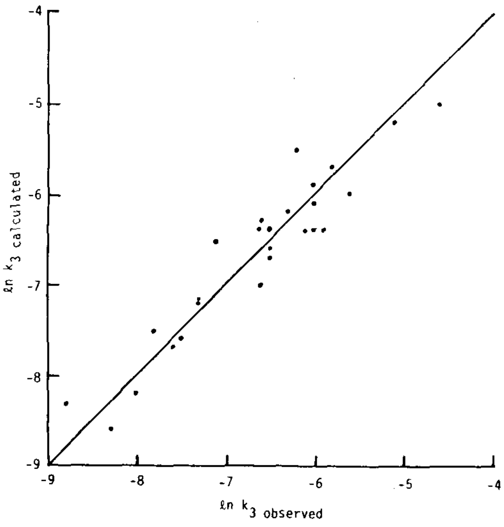

**FIG. 3. Calculated values vs observed values of $k_3$.**

tivity should be reduced when pressure is increased. These suggestions agree with common knowledge in hydrogenation (3,4). Further, our selectivity model presents a quantitative means to predict selectivity according to the process variables. These models should have significant value to the processor.

Inspection of the SR model reveals that selectivity is independent of $P_0$. Since $k_2$ and $k_3$ are both affected by $P_0$ to the same degree, the influence of power/unit volume to SR is cancelled out when the ratio of $k_2$ vs $k_3$ is considered. It should be cautioned, though, that SR is still a function of the level of hydrogen in oil as expressed by the pressure term. But, when compared to Equations V, VI and VII, the pressure effect in the SR equation is rather small.

The influence of temperature, catalyst concentration and hydrogen pressure on SR is graphically demonstrated in Figure 4. In this figure, SR is plotted against temperature as the catalyst level, power/unit volume and hydrogen pressure are held at the middle point values, i.e., 1,200 ppm, 0.034 HP/ft$^3$ and 26 psig, respectively. When SR was plotted against catalyst or pressure, similar approaches were taken.

Comparison of Equations IX and X reveals that SR is a much stronger function of the process parameters than LnSR. It is known that LnSR is independent of the process parameters; therefore, the linolenic selectivity model as shown in Equation IX merely represents the composite error due to modeling and experimental procedure.

### Activation Energy ($E_a$)

$E_a$ as shown in Equation I can be obtained as follows: first equate $E_a/RT$ of Equation I to $b_1/T$ of Equation II, then solve for $E_a$ in terms of $b_1$ and R. It can be seen that $E_a$ is equal to $b_1$ times R. The values of $E_a$ for $k_1$, $k_2$ and $k_3$, obtained from this approach, range from 7 to 12 kcal/mol, which agrees well with values suggested by the catalyst manufacturer and the literature (12). However, caution should be taken when this approach is used. As discussed by Glass tone and coworkers (5), the activation energy and frequency factor are dependent on each other; $E_a$ is affected by A as in Equation I. Inspection of Equation II shows that the constant $b_1$ is affected by the constant $b_0$, as well as by $b_2$, $b_3$ and $b_4$. Therefore, if activation energy is calculated from $b_1$, this value should be considered as an approximation or a pseudo-value.

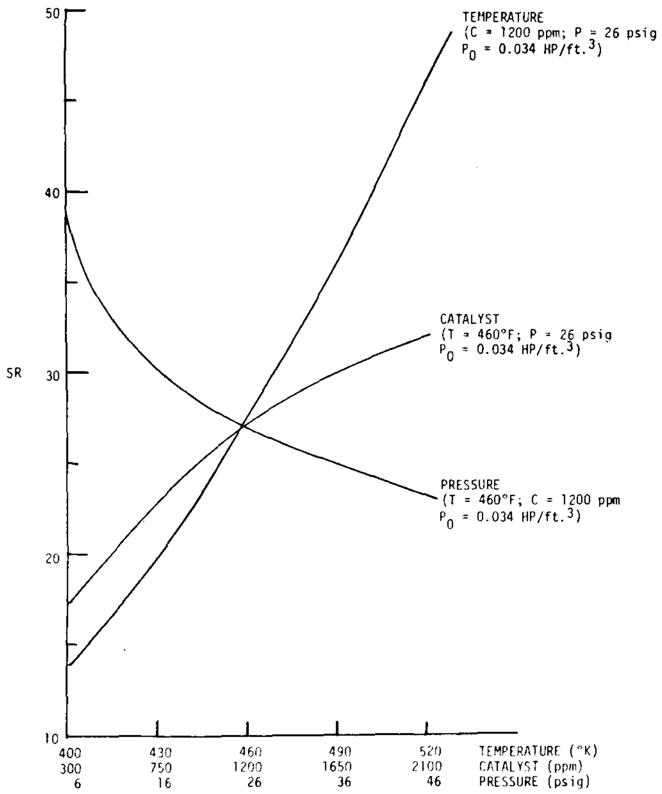

**FIG. 4. Selectivity of linoleic vs temperature, catalyst concentration and hydrogen pressure.**

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