Investigation and Modeling of Mass Transfer in Soybean Oil Hydrogenators[1]

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ABSTRACT

The volumetric mass transfer coefficient (k_La) for soybean oil hydrogenation was determined from various sizes of hydrogenators, 0.2 kg, 45.5 kg, 455 kg, 15454 kg and 29100 kg. The 0.2 kg bench hydrogenator was shown to simulate and to approximate the gas/liquid mass transfer resistance of the production hydrogenator. The activation energy for the production simulation of 7.2 kcal/mole, indicating the hydrogenation is strongly influenced by mass transfer. A mathematic model was constructed for the prediction of k_La when the calculated power per unit volume of oil (P/V), the ratio of the oil height vs hydrogenator diameter (H/T) and the Raynold's number of the agitator (N_{Re}) are known. Production data obtained from the literature were used for testing the validity of the model; the maximum deviation was found to be 12%. Practical applications by using this model are also discussed.

INTRODUCTION

The control of hydrogen transfer in hydrogenation has a tremendous impact on the quality of hydrogenated vegetable oils as well as on the economics. In hydrogenation, the rate controlling step can be either mass transfer or kinetics; however, most of the hydrogenators in vegetable oil production are operated within the mass transfer controlling region. Roberts (1) and Coenen (2) presented excellent reviews in this area.

Hydrogenation of an oil is affected by four parameters: temperature, hydrogen pressure, type and concentration of catalyst, and degree of agitation. Since the degree of agitation is the only extensive parameter, i.e., the degree of agitation depends on specific reactor design, particular attention should be given to this area when scale-up or scale-down is performed. Many authors characterized the degree of agitation by the use of k_La. k_L is the mass transfer coefficient for the liquid film which is commonly treated as constant within a specified system; whereas "a" is the interfacial area of the hydrogen bubbles per unit volume of oil which is greatly affected by the degree of agitation. The use of k_La for the purpose of agitation measurement is merely a convenience because the determination of "a" alone can be tedious and is sometimes impossible.

An excellent review article relating k_La to agitation was presented by Sideman et al. (3). Of particular interest, Bern et al. (4) studied the mass transfer and scale-up of rapeseed oil hydrogenation with three different sizes of reactors which had similar geometry, and showed that k_La could be expressed through the diameter and the rpm of the agitator, the volume of oil, and the linear gas velocity of hydrogen. Unfortunately, in the fats and oils industry, most of the bench and pilot plant hydrogenators are not necessarily scaled-down from the production reactors; therefore, the approach proposed by Bern et al. cannot be applied.

The purpose of the present paper is to illustrate a technique in which the degree of agitation, through the expression of k_La, can be correlated with three intensive parameters: P/V, H/T and N_{Re}. Since the correlation was developed from five reactors ranging from 0.1 kg to 29,100 kg in capacities and with dissimilar designs, this technique should be useful to the fellow processors who routinely deal with scale-up and production simulation.

EXPERIMENTAL PROCEDURES

Hydrogenators and Hydrogenation

Hydrogenators with 5 various sizes were used. They were: 0.2 kg bench unit, 45.5 kg and 455 kg pilot plant units, 15,454 kg and 29,100 kg production units. The designs of these hydrogenators are given in Table I. As can be seen in this table, the designs of these hydrogenators do not bear any geometric similarity, except for the two production units. During this investigation, various k_La values were obtained by varying the rpm of the bench and pilot plant units. However, it was found that the 455 kg pilot unit did not give a significantly different k_La when the agitator rpm was changed; therefore, the volume of oil used was varied instead. Three different volumes of oil were employed. They were: 455 kg, 273 kg and 182 kg. The two production units were equipped with single speed motors and the rpm did not vary during this study.

Only soybean oil was investigated for the current work. The nickel catalyst (Nysel) from Harshaw Chemical at 0.1% concentration was used throughout the k_La experiments,

TABLE I

Design of Hydrogenators

Hydrogenator (kg)	0.2	45.5	455	15,454	29,100
Height of oil / Hydrogenator dia	0.28	4.2	0.83	1.5	1.5
Hydrogenator dia.	9.8 cm	25.4 cm	91.4 cm	2.44 m	3.05 m
Baffle	no	no	no	yes	yes
Type of agitator	45° pitch turbine	6 disc blade	6 disc blade	5 disc blade	5 disc blade
Agitator rpm	100-600	96-384	190-230	125	100
Dia. of agitator (cm)	3.2	15.2	35.6	37.1	91.4
No. of agitator	1	1	1	3	3

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except for the production simulation and the activation energy measurements using the bench unit, where the concentration of catalyst was varied from 0.01% to 0.1%. All catalyst concentrations were based on nickel content. The progress of the hydrogenation was followed by the refractive index measurement of the oil, and the iodine value (IV) was converted from this refractive index measurement.

Calculation of k_La

In hydrogenation, the overall rate controlling step can be either the mass transfer of hydrogen or the kinetics of the reaction. However, in order properly to characterize the degree of agitation through the measurement of k_La, the hydrogenation process has to be manipulated in such a way that the rate controlling step is solely governed by the transport of the hydrogen. This situation can be easily achieved through the high loading of catalyst. For the readers who are not familiar with this technique, the Roberts' (1) article should be of some help.

In k_La determination, the rate of reaction and the conditions under which the hydrogenation is carried out have to be known. The rate of reaction can be measured and is commonly expressed in IV/min. In the present work, the rate in IV/min was determined by drawing a linear line from the IV vs min plot between 132 IV and 110 IV. The ranges of temperature and pressure used in the experiment were 162-121 C and 0.34 to 1.35 atm respectively. The bench and the two pilot plant hydrogenators were operated isothermally, but the two production units were run according to the adiabatic mode, as are most of the production hydrogenators operated in the USA. Since the plots for the IV vs min were linear for all the experimental runs within the 132-110 IV range, the arithmetic average of temperature for the two production units was used in the calculation. Bern et al. showed that k_La can be expressed through the rate of hydrogenation and the solubility of hydrogen (4). The present study followed Bern et al.'s approach for calculating k_La (4).

To determine the solubility of hydrogen in oil, the hydrogen pressure and temperature are required. The solubility calculation in this paper used the equation suggested by Andersson et al. (5). This equation was obtained from the solubility measurement of hydrogen in cottonseed oil. In the present work the hydrogen pressure was measured at the head space of the hydrogenator. Since the hydrogen pressure measured at the bottom of a tall hydrogenator can be different from that measured at the head space, a correction was made for the effect of the hydrostatic head on the hydrogen pressure on the production units (6). For the bench and pilot plant units, this correction proved to be unnecessary.

Modeling of k_La

As previously mentioned, the validity of Bern et al.'s modeling approach (4), which relates k_La to the operating parameters, i.e., agitator rpm, agitator diameter, volume of oil and hydrogen gas flow rate, is restricted to the hydrogenators having similar geometry. This restriction can be a real problem to the processors who possess bench, pilot plant and production units with dissimilar designs. The authors, therefore, propose a model in which the parameters are either intensive or dimensionless. This will allow valid scale-up and scale-down without the restriction of geometric similarity. Further, this approach will offer reliable interpolation which is frequently required in industrial research.

The parameters for the current k_La model are: P/V, N_{Re} and H/T. P/V is in watt/m^3 and both N_{Re} and H/T are dimensionless. The validity of the use of P/V to characterize the degree of agitation has been thoroughly reviewed and demonstrated (7). Recently, Chen et al. (8) showed that P/V was an important parameter in the modeling of hydrogenation rate constants for soybean oil. The power input, or P, for the present study was calculated as suggested in the literature (9). The effect of the gas flow on the power input was accounted for according to the same literature. The gas flow rate was calculated by converting the hydrogenation rate in IV/min into proper volumetric gas flow rate (10). The density and viscosity data required for the power calculation obtained from the literature (11,12). N_{Re} is commonly used to characterize agitation due to the consideration of fluid mechanics in chemical engineering (9). The definition of N_{Re} is given as follows:

$$N_{Re} = \frac{D^2 n \rho}{\mu} \quad [1]$$

where D is diameter of agitator, n is revolution per second of agitator, ρ is density of oil and μ is viscosity of oil. The use of H/T allows for the geometry effect in dissimilar hydrogenator design.

RESULTS AND DISCUSSION

k_La and Activation Energy

The k_La values obtained for the bench and pilot plant units by varying the rpm of the agitators are shown in Figures 1 and 2. As can be seen from these curves, the k_La increases as agitation increases. The k_La values vs various batch sizes for the 455 kg hydrogenator are depicted in Figure 3. The k_La decreases as batch size increases.

The k_La measured from the 29,100 kg and 15,454 kg production hydrogenators were found to range from 0.14 to 0.18 sec^{-1}, respectively. Inspections of Figures 1-3 indicate that the production units can be simulated with the bench and both pilot plant hydrogenators. It was then decided that the bench unit should be used to simulate the production hydrogenator with 0.143 sec^{-1} k_La value for two reasons: to determine the degree of mass transfer resistance due to gas/liquid phase, and to obtain the activation energy which would substantiate such a mass transfer determination.

The production simulation was performed according to the following procedure: the rpm of the bench agitator was set at the value where the k_La would match the production unit; the pressure of the bench hydrogenator was operated

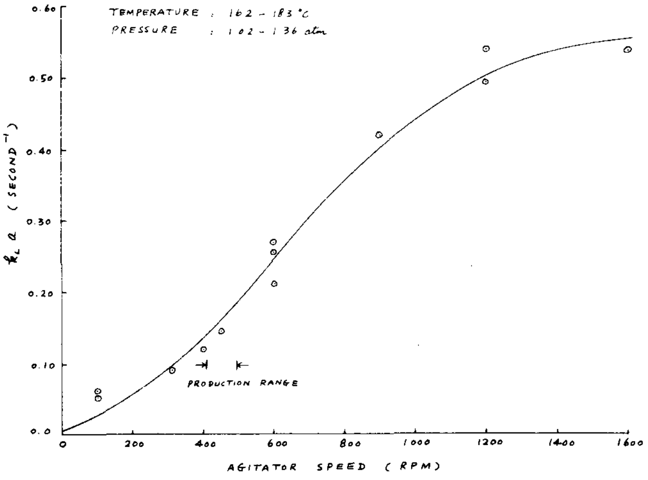

FIG. 1. k_La vs agitator speed of 0.2 kg hydrogenator.

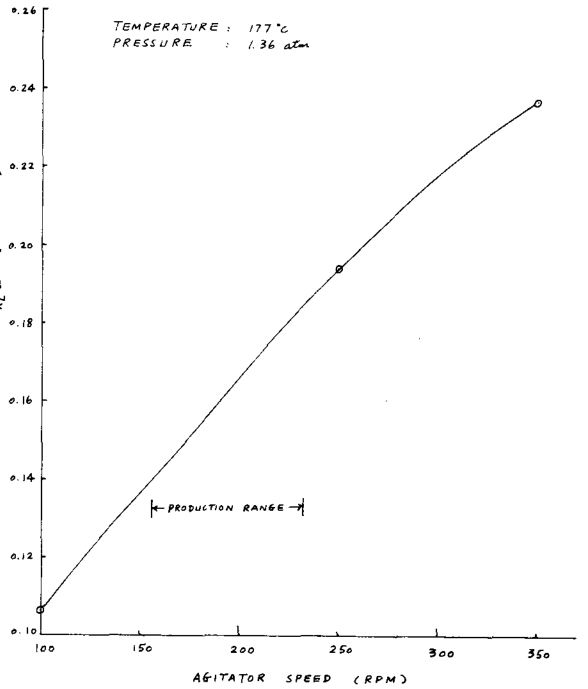

FIG. 2. k_La vs agitator speed of 45.5 kg hydrogenator.

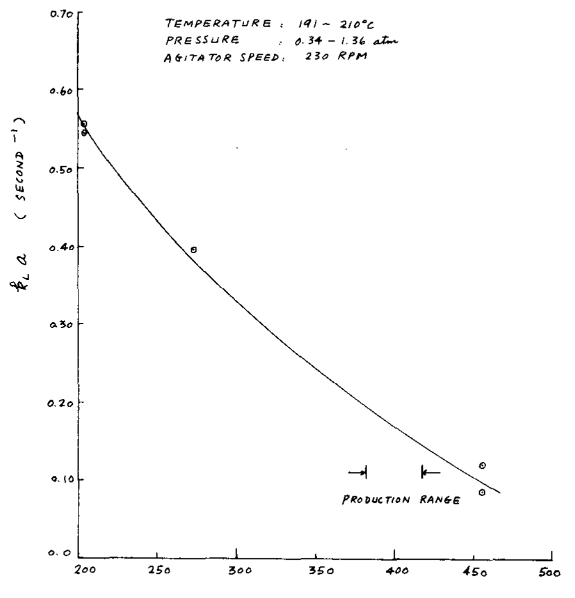

FIG. 3. k_La vs batch size of 455 kg hydrogenator.

according to the production setting. Since plant operation is adiabatic, the heater of the bench unit was properly programmed so that a temperature rise similar to the production hydrogenator could be obtained. Four different loadings of catalyst were used; they were: 0.1%, 0.05%, 0.02% and 0.01%.

According to Roberts (1), the plot of the reciprocal of the rate of hydrogenation vs the reciprocal of loading of catalyst will allow the determination of the percent of mass transfer resistance due to the gas/liquid phase. Figure 4 depicts such a plot. In Figure 4, N is the rate of hydrogenation in mole H_2/L oil-sec, and W is the catalyst loading in g. As can be seen from this figure, the gas/liquid phase resistance in comparison to the total resistance, increases as the loading of catalyst increases. In typical production operation, the levels of catalyst range from 0.01 to 0.08% depending on the type of products to be made. The corresponding gas/liquid phase resistances in comparison to the total resistance are 56% and 90%, respectively.

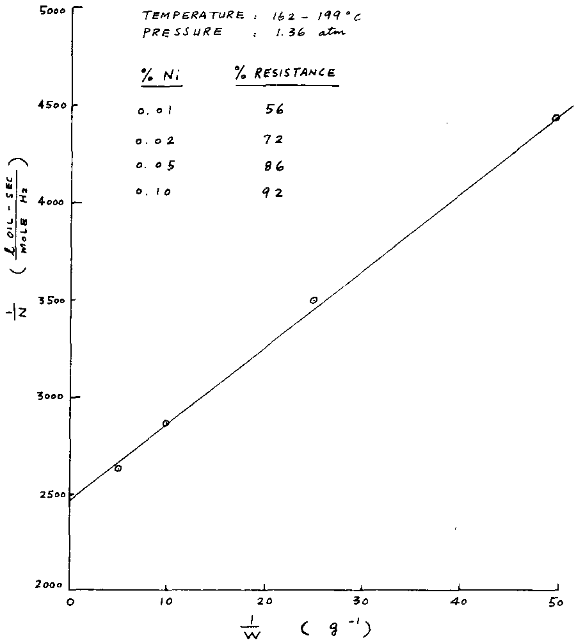

FIG. 4. Determination of mass transfer resistance due to gas/liquid phase.

The activation energy for the production hydrogenator was obtained by using the bench unit as simulator. The procedure used was identical to the mass transfer simulation previously mentioned, except the reactions were carried out under isothermal conditions. Three temperatures were used, namely, 163 C, 199 C, and 232 C, which covered the full temperature range of the production hydrogenation. The catalyst loading was 0.02%. The Arrhenius plot shown in Figure 5 and the activation energy was estimated as 7.2 kcal/mole. Roberts (1) suggested that if the activation energy is greater than 10 kcal/mole, the reaction is controlled by kinetics; likewise, the reaction is governed by mass transfer when the corresponding activation energy is 5 kcal/mole or less. Since the activation energy for this simulation is 7.2 kcal/mole, this indicates that the hydrogenation is highly influenced by mass transfer. In Figure 4 the mass transfer caused by gas/liquid phase transport is shown to be 72% at 0.02% catalyst loading. This further suggests the overall hydrogenation rate is controlled by the mass transfer of hydrogen. It is comforting to know that two independent techniques resulted in a similar finding – hydrogenation is highly influenced by the mass transfer of hydrogen.

k_La Modeling

The k_La values obtained from the bench, pilot plant and production hydrogenators and their corresponding P/V, N_{Re} and H/T values range from 0.054 to 0.77 sec^{-1}, 10 to 43,767 watt/m^3, 1465 to 579,278 and 0.28 to 1.5, respectively. These values with the k_La as the dependent variable and the P/V, N_{Re} and H/T as the independent variables were fitted according to the power series model as commonly practiced in chemical engineering (13). The correlation coefficient (R) was rather low for this model, suggesting the data can-

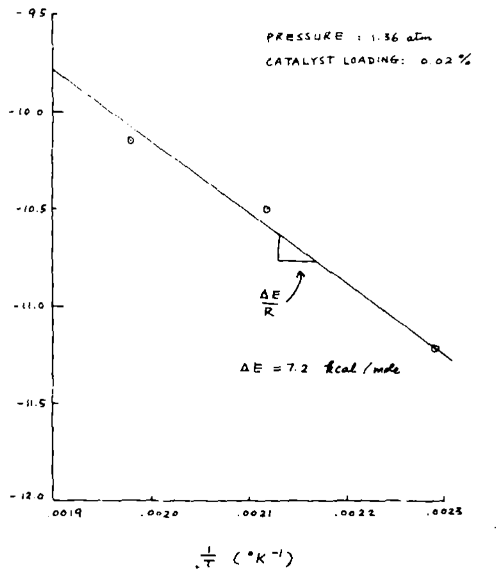

FIG. 5. Arrhenius plot of production simulation.

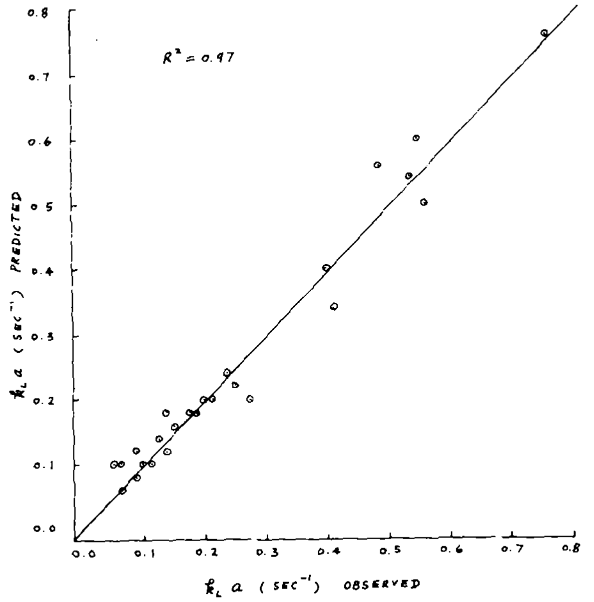

FIG. 6. Predicted k_La vs observed k_La.

not be fitted with the power series. Subsequently, a polynomial model was tried. The selection of the terms in the model was based on the technique of "maximum R^2 improvement" (14). The resulting model is given as follows:

$$k_La = 0.5208 + 5.206 \times 10^{-6} (N_{Re}) + 4.055 \times 10^{-5} (P/V) - 1.699 (H/T) - 1.092 \times 10^{-9} (N_{Re}) (P/V) - 5.221 \times 10^{-12} (N_{Re})^2 + 8.064 \times 10^{-11} (P/V)^2 + 0.4826 (H/T)^2 \qquad [2]$$

The R^2 of this model is 0.97, indicating 97% of the deviations are explained by the model; the model fitted the data extremely well. The observed k_La were plotted against their predicted values from the model in Figure 6. Again, this plot confirms that the model is satisfactory.

It is recognized that the polynomial form of the model cannot give physical significance to the system investigated. However, the intention of the present study is to provide a procedure for scale-up or scale-down; the good fit of the model to the data alone should justify the choice of such a model. The proper use of this model should result in much valuable and practical information regarding production, pilot plant and bench hydrogenations, as illustrated in the following section.

Bern et al. (4) developed a scale-up equation by using the two pilot hydrogenators with 24 kg and 400 kg capacities. The scale-up equation was then used to predict three production runs from a geometrically similar hydrogenator with 19,200 kg capacity. The results of the prediction are shown in Table III.

The model as illustrated in Equation 2, was tested with Bern et al.'s data and the results are shown in Table III. Inspection of this table indicated that the prediction from Equation 2 is more accurate than from Bern's model; the maximum deviations by using Equation 2 vs Bern et al.'s are 12% vs 30%, respectively. Since the model by Bern was constructed from two hydrogenators with 24 kg and 400 kg capacity, and the production hydrogenator tested had the capacity of 19,200 kg; the prediction of this production unit required extrapolation of the model. On the contrary, the model derived by the authors was based on five hydrogenators ranging from 0.2 kg to 29,100 kg. The prediction for Bern et al.'s 19,200 kg hydrogenator by using the present model is a matter of interpolation. The authors believe this is the main reason for their model's superiority over Bern et al.'s model.

Application of Model

As discussed previously, hydrogenation of an oil is affected

TABLE II

Comparison of Predictions from Bern et al.'s vs Chen et al.'s Models

Bern et al.'s hydrogenators (4):

Hydrogenator diameter = 2.4 m
Agitator diameter = 0.9 m
rpm of agitator = 75
Hydrogenation pressure = 1.4 atm
Hydrogenation temperature = 180 C

Run no.	1	2	3
IV/min	0.5	0.61	0.65
Oil volume (m^3)	11.06	14.74	11.67
k_La experimental (sec^{-1})	0.043	0.052	0.056
k_La predicated by Bern (sec^{-1})	0.042	0.039	0.039
k_La predicted by Chen (sec^{-1})	0.047	0.058	0.062

by: temperature, hydrogen pressure, type and concentration of catalyst, and degree of agitation. Except for the degree of agitation, all the other parameters are intensive. The proper use of the present model will allow one to have a handle on the degree of agitation, therefore making the hydrogenation process manageable. Following are the typical examples where some practical applications of the model, as shown in Equation 2, are illustrated.

Characterization of hydrogenator. In production as well as in research and development, it is essential to be able to characterize the hydrogenator used and to determine the agitation for each hydrogenator. The degree of agitation can be calculated from Equation 2 directly. Once the degree of agitation for the hydrogenator has been assessed, agitation among different hydrogenators can be easily compared. Of course a similar assessment can be done by the actual experimentation such as illustrated in the present paper; however, the use of Equation 2 should allow one to omit the performance of the experiment.

Scale-up. It is a nightmare of all R & D personnel not to be able to scale-up from the bench or pilot plant to the production. The proposed model should be helpful in this respect. If scale-up from the bench unit to the production hydrogenator is the concern, Equation 2 should be used to estimate the k_La or the degree of agitation for both hydrogenators. If the production unit for some reason has more agitation than the bench unit, the operating condition of the bench unit should be changed so that the k_La for both of the hydrogenators are matched. This can be achieved by either increasing the rpm of the bench agitator or reducing the amount of oil used for the bench unit. In any case, the proposed model should be used as a guideline for making these changes.

Simulation. In production environment, the what-if questions are often brought up. What if we speed up the rpm of the agitator? What if we hydrogenate oil with higher viscosity? What if we increase the batch size to improve productivity? These questions can be answered if one uses the proposed model. For example, if bigger batch size in production is desired, a corresponding k_La for this situation can be estimated by using Equation 2. Then, the bench unit should be employed to simulate the new k_La. The selectivity and other quality attributes of hydrogenated oil from the bench experiment should be assessed prior to making changes in the production.

ACKNOWLEDGMENT

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ERRATA

In the article "Instrumentation in Vegetable Oil Processing" appearing in the March issue of *JAOCS* (Farr 60:571 [1983]), an error exists on page 573. In the formula

$$V = \frac{GPM \times 0.048}{d^2},$$

"d = diameter of tube (ft)" is incorrect. It should read "d = diameter of tube (in.)".

In the April 1983 issue of *JAOCS*, pages 836 and 838 were inadvertently misnumbered and consequently switched. Page 836 should be numbered 838, and vice versa.