Quantitative Measure of Geometrical Isomerization During the Partial Hydrogenation of Triglyceride Oils

LYLE F. ALBRIGHT, Purdue University, Lafayette, Indiana, ROBERT R. ALLEN and M. C. MOORE, Anderson-Clayton Foods, Richardson, Texas

Abstract

A mathematical model has been developed using a digital computer for the calculation of the isomerization index for partially hydrogenated oils such as cottonseed, soybean, peanut or corn oil. The isomerization index is defined as the ratio of the rate of geometrical isomerization of an unsaturated group to the rate of hydrogenation. Isomerization indices from about 0.3 to 11 were found to occur for hydrogenations using commercial nickel catalysts. Calculation of both an isomerization index and a selectivity ratio will be useful methods of quantitatively characterizing the partial hydrogenation of triglyceride oils or the type of hydrogenation which can be obtained by various catalysts.

Quantitative Measure of Geometrical Isomerization During the Hydrogenation of Triglyceride Oils

Many simultaneous and consecutive reactions occur during the hydrogenation of triglyceride oils (1,2,5,6–9,14; also, Allen, personal communication). Some double bonds are saturated with hydrogen while other double bonds are isomerized both positionally and geometrically. The isomerized double bonds may later hydrogenate or be further isomerized. Variations in the relative rates of the hydrogenation and isomerization reactions have a significant effect on the properties of the hydrogenated product.

Various models for the reaction sequence have been proposed in the past (3,5,7,8,10,12). The following simple model for example is useful for measuring the selectivity ratio (SR), i.e., the degree of selectivity that occurs during hydrogenation (3):

$$\begin{pmatrix}\text{Triunsaturated}\\ \text{fatty acid}\\ \text{groups}\end{pmatrix} \xrightarrow{k_a} \begin{pmatrix}\text{Diunsaturated}\\ \text{fatty acid}\\ \text{groups}\end{pmatrix} \xrightarrow{k_b} \qquad [1]$$

$$\begin{pmatrix}\text{Monounsaturated}\\ \text{fatty acid}\\ \text{groups}\end{pmatrix} \xrightarrow{k_c} \begin{pmatrix}\text{Saturated}\\ \text{fatty acid}\\ \text{groups}\end{pmatrix}$$

Mathematical equations were developed based on the assumption that each of the three hydrogenation steps shown above is irreversible and first order; rate constants for each step are designated as k_a, k_b, k_c, respectively. These equations were used by substituting the compositions of the main body of the liquid (or oil) phase and not the actual compositions at the catalyst surface, where the reactions actually occur. Consequently the rate constants determined are pseudo and not true chemical rate constants. The selectivity ratio is often defined as the ratio of the rate constants for hydrogenation of the diunsaturated acid groups to those of the monounsaturated groups, i.e., k_b/k_c. Such a ratio is of importance in characterizing the selectivity for hydrogenations using catalysts such as nickel, platinum or palladium. Such catalysts are quite effective for the hydrogenation of monounsaturated groups but are even more effective for polyunsaturated groups. A selectivity ratio of k_a/k_b is useful for runs in which the major hydrogenation reactions are of the triunsaturated groups, but less unsaturated groups are hydrogenated to only a small extent. Copper chromite catalysts are effective for such hydrogenations.

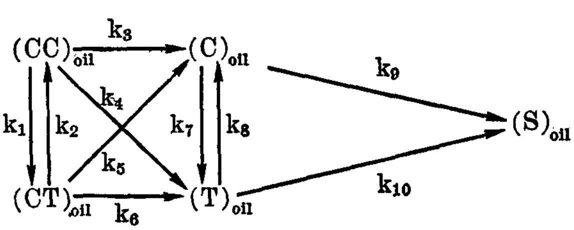
Geometrical isomerization that occurs during the partial hydrogenation of triglyceride oils is known to have a pronounced effect on the physical properties of the hydrogenated product. The present paper describes a method which can be used to compare the rates of isomerization and of saturation of the double bonds in oils such as cottonseed, corn and soybean oils.

Procedure Used to Develop Isomerization Model

The isomerization model proposed is specifically for triglycerides that contain diunsaturated, monounsaturated and saturated fatty acid groups. As will be discussed later, the model can also be used for oils that contain some triunsaturated groups. In the model, the fatty acid groups are divided into five families: (a) *cis-cis*-diunsaturates (CC); (b) *cis,trans*-diunsaturates (CT); (c) *cis*-monounsaturates (C); (d) *trans*-monounsaturates (T); (e) saturates (S).

Some *trans,trans*-diunsaturated groups (TT) may also occur, but the amounts of TT are likely quite small. Inclusion of TT in the model would seriously complicate the model which is already highly complicated. As a result, TT was not included. Subsequently it was found that such an omission had no deteremental effects on the final model and that CT always hydrogenated to T just as TT would be expected to do.

Mathematical equations were developed for the following model for CC, CT, C, T and S as a function of time (t) based on the assumption that each of the 10 reaction steps shown follows first order kinetics based on the total amount of that family in the oil:



[2]

These equations are as follows:

$$CC = X_1EXL_1 + X_2EXL_2$$
$$CT = Y_1EXL_1 + Y_2EXL_2$$
$$C = P_1EXL_1 + P_2EXL_2 + D_1EXL_3 + D_2EXL_4$$
$$T = P_3EXL_1 + P_4EXL_2 + D_3EXL_3 + D_4EXL_4$$
$$S = CC_o + CT_o + C_o + T_o + S_o - CC - CT - C - T$$

where $EXL_1 = e^{XL_1 t}$; $EXL_2 = e^{XL_2 t}$; $EXL_3 = e^{XL_3 t}$; $EXL_4 = e^{XL_4 t}$; $XL_1 = 0.5(CP_1 - B_1)$; $XL_2 = -0.5(CP_1 + B_1)$; $XL_3 = 0.5(CP_2 - B_2)$; $XL_4 = -0.5(CP_2 + B_2)$; $CP_1 = (B_1^2 - 4C_1)^{0.5}$; $CP_2 = (B_2^2 - 4C_2)^{0.5}$; $B_1 = k_1 + k_2 + k_3 + k_4 + k_5 + k_6$; $B_2 = k_7 + k_8 + k_9 + k_{10}$; $C_1 = [(k_1 + k_3 + k_4)\ (k_2 + k_5 + k_6) - k_1]k_2$; $C_2 = [(k_7 + k_9)\ (k_8 + k_{10}) - k_7]k_8$;

$D_1 = [k_3CC_o + k_5CT_o - (k_7 + k_9 + XL_4)\ C_o + k_8T_o + (XL_4 - XL_1)P_1 + (XL_4 - XL_2)P_2]/(XL_3 - XL_4)$; $D_2 = C_o - P_1 - P_2 - D_1$; $D_3 = [k_6CT_o + k_4CC_o - (k_8 + k_{10} + XL_4)T_o + k_7C_o + (XL_4 - XL_1)P_3 + (XL_4 - XL_2)P_4]/(XL_3 - XL_4)$; $D_4 = T_o - P_3 - P_4 - D_3$; $X_1 = [k_2CT_o - (k_1 + k_3 + k_4 + XL_2)CC_o]/(XL_1 - XL_2)$; $X_2 = CC_o - X_1$; $X_3 = [k_1CC_o - (k_2 + k_5 + k_6 + XL_2)CT_o]/(XL_1 - XL_2)$; $X_4 = CT_o - X_3$; $Z_1 = (k_8 + k_{10} + XL_1)\ (k_3X_1 + k_5X_3) + k_8(k_4X_1 + k_6X_3)$; $Z_2 = (k_8 + k_{10} + XL_2)\ (k_3X_2 + k_5X_4) + k_8(k_4X_2 + k_6X_4)$; $Z_3 = (k_7 + k_9 + XL_1)\ (k_6X_3 + k_4X_1) + k_7(k_5X_3 + k_3X_1)$; $Z_4 = (k_7 + k_9 + XL_2)\ (k_6X_4 + k_4X_2) + k_7(k_5X_4 + k_3X_2)$; $P_1 = Z_1/(XL_1^2 + B_2XL_1 + C_2)$; $P_2 = Z_2/(XL_2^2 + B_2XL_2 + C_2)$; $P_3 = Z_3P_1/Z_1$; $P_4 = Z_4P_2/Z_2$.

The composition of each family is expressed as a weight per cent in the oil. (Actually the compositions in these equations should be expressed as mole per cent, but weight per cent is essentially identical to mole per cent for triglycerides.) The equations include time terms; rate constants (k's); and compositions of the starting oil expressed as CC_o, CT_o, C_o, T_o, and S_o. In testing various experimental data, the total trans content of the starting oil was assumed to occur completely in the monounsaturated acid group, or at T.

When applied to experimental data, values of the true time of the run or pseudo time can be used in the above equation. Pseudo time is defined here as the arbitrary choice of a range of values for time, and these latter were used for at least two reasons: (a) An induction period frequently occurs in hydrogenation runs, so that no linear correlations exist between the actual times of hydrogenation and the pseudo times. These induction periods frequently result because the activity of the catalyst increases during the initial stages of a run (4). (b) Using pseudo times permits comparisons between two or more hydrogenated products regardless of the actual times for hydrogenation employed in each case.

An extensive trial-and-error procedure was used to determine the following: (a) Values for k_1 through k_{10}. (b) A method of calculating the iodine value (IV) of the final product. (c) A procedure for predicting the *trans* content of the final oil.

In making these calculations, the Purdue University IBM 7094 digital computer was employed. For a given set of k values, the composition of the hydrogenated oil was calculated at numerous values of pseudo time. Methods of calculating the IV and the *trans* acid content of the final product were then tested.

Proposed Isomerization Model

The model developed can be used to represent experimental hydrogenation data over a wide range of SR values and of II (isomerization index) values. The isomerization index will be defined later. The following pseudo reaction rate constants are applicable to the proposed model: $k_3 = 1.0$ (set arbitrarily); $k_6 = 1.0$; $k_4 = k_5 = 0.0$; $k_1/k_2 = 3.0$; $k_7/k_8 = 3.0$; $k_9 = k_{10}$.

Setting k_1/k_2 and k_7/k_8 equal to 3.0 is based on the results of Litchfield et al. (12) who found that the equilibrium ratio of *trans* to *cis* double bonds was about 3. Values of 2 have sometimes been used for this equilibrium ratio, but the larger value is probably more accurate in most cases. Equating k_3 and k_6 and equating k_9 and k_{10} are at least good approximations based on experimental hydrogenation results.

The CC is considered to be hydrogenated only to C. One might reason that the hydrogenation of one double bond and the isomerization of the other double bond would not occur simultaneously. Hydrogenation of CT to only T is not as easy to explain. It is known that the starting nonconjugated diene often isomerizes positionally to a conjugated diene (7). Certainly more research is needed to obtain additional information on the steps involved in hydrogenation and isomerization of diunsaturated groups.

The proposed model is really an expansion of the selectivity model proposed earlier (3). Inspection of the isomerization model indicates that $k_3/k_9 = k_6/k_{10}$. Furthermore k_3/k_9 equals k_b/k_c of Equation 1 so that

$$SR = k_b/k_c = k_3/k_9 = k_6/k_{10} \tag{3}$$

Since SR can be determined for a given hydrogenation (3), k_9 and k_{10} are then set.

The isomerization index (II) is defined as the ratio of the rate of geometrical isomerization to the rate of hydrogenation for both CC and C. Consideration was given to designating the term as either the isomerization ratio or as the isomerization value. The abbreviations for these would however be confused with those for infrared and iodine values respectively. Mathematically II is expressed as follows:

$$II = \frac{\text{Rate of geometrical isomerization of CC}}{\text{Rate of hydrogenation of CC}} = \frac{k_1(CC)}{k_3(CC)} = \frac{k_1}{k_3} \tag{5}$$

$$II = \frac{\text{Rate of geometrical isomerization of C}}{\text{Rate of hydrogenation of C}} = \frac{k_7(C)}{k_9(C)} = \frac{k_7}{k_9} \tag{4}$$

$$II = k_1/k_3 = k_7/k_9 \tag{6}$$

Since the concentration of hydrogen at the catalyst surface is of course identical for the simultaneous reactions of CC and C above, it seems quite reasonable to expect that k_1/k_3 is at least approximately equal to k_7/k_9. However there is as yet no direct experimental evidence to prove this postulate.

Several values of k_1 were then assumed, and values of II, k_7 and all other k's could then be calculated at a given selectivity ratio. Methods of calculating the IV and the *trans* acid content of the hydrogenated oil had to be developed next.

The IV was calculated as follows:

$$IV = 0.8601\ (C + T) + 1.732\ (CC + CT) \tag{7}$$

This method seems at first to be routine, based on the IV of pure C, T, CC and CT expressed in weight per cent. It should be pointed out, however, that very high CT values are often obtained by the calculation procedure used. Such high values probably give reasonably good indications of the compositions actually present on the catalyst surfaces, but it is known that such high values do not occur in the main body of the oil. It does seem reasonable however that the sums of CC and CT would be equal to the amounts of diunsaturates present in the oil phase.

Calculation of the total *trans* acid content of the final oil involves several assumptions since both T and CT contribute to the total. Only part of the CT formed on the surface of the catalyst is desorbed and transferred to the main body of the oil. However a considerably larger fraction of T is desorbed since T is less strongly adsorbed on the catalyst surface. It was assumed that all of T, as calculated by these equations, contributed to the *trans* content but that only a fraction (F) of CT did. A trial-and-error procedure was used to develop an expression for F to be used for cottonseed oil hydrogenations:

$$F = 0.4 - 0.012\,(CT) \qquad [8]$$

F probably actually increases as the hydrogenation progresses. Based on equilibrium considerations, F would be expected to be highest for the largest surface concentrations of CT. Because of mass transfer resistances however, F becomes greater when the net transfer of CT is from the oil phase to the catalyst surface, i.e., at lower IV. The above empirical equation is thought to be a fair approximation of F in the range from about 95 IV to lower values. The equation used to calculate the total *trans* groups (expressed on a *trans* monosaturated fatty acid basis) in the hydrogenated oil is as follows:

$$Trans = T + (0.4 - 0.012(CT))\,CT \qquad [9]$$

Testing of Model

Calculations were made for numerous hydrogenations of cottonseed oils with the expanded model for hydrogenation over the ranges: SR: 2 to 100; II: 0.2 to 20.

Curves of the calculated *trans* contents were plotted versus IV; these curves were similar in shape to those obtained experimentally. Plots at a given II changed to only a small extent, as SR varied. Experimental results for a batch run at a given set of operating variables (temperature, pressure and degree of agitation) generally resulted in reasonably constant SR and II values throughout the course of the run especially if smoothed data for the run were used. It should be emphasized that SR and II can be measured most accurately in the range from 50 to 80 IV for most hydrogenations. A small analytical error of the diunsaturated group or the *trans* group content would result in rather appreciable changes in the value of SR or II respectively at IV outside this range. Table I shows SR and II values for oil samples obtained during hydrogenations of cottonseed oil at very low SR (14), for intermediate SR (13), and for high SR (Allen, personal communication), respectively. The ratio of SR to II was generally found to be within the range of 2 to 12 for these hydrogenations using commercial nickel catalysts.

The isomerization model was also tested for oils such as soybean oil that contain relatively small amounts of triunsaturates. The diunsaturates and triunsaturates in the original oil were grouped to calculate a pseudo diunsaturate composition designated as CC′ for the starting oil:

$$CC' = (\text{Diunsaturates}) + 1.5\,(\text{Triunsaturates}) \qquad [10]$$

CC′ was then used in the model in place of CC. Details on the method of calculating SR and II for hydrogenations of soybean oil will be discussed later. Table II shows SR and II values for several runs made using soybean oils and two commercial nickel catalysts. The values of both SR and II are considered to be less accurate at IV above 90, and the ratio of SR to II is considered to be less accurate in such cases. It would appear, based on Table II, that Nysel catalyst obtained from Harshaw Chemical Co. tends to give higher values of II than does G-15 catalyst obtained from Girdler Catalysts Department of Chemetron Corporation.

Use of Isomerization Model

Both SR and II values can be determined for a hydrogenated product obtained from cottonseed, corn, soybean or similar oil if (a) composition of initial (unhydrogenated) oil and (b) composition of the partially hydrogenated oil are available. If the composition of the initial oil is not known, an average composition may be assumed.

The calculation procedure recommended for cottonseed, corn or peanut oils is as follows:

(a) Determine the approximate SR value using the procedure outlined by Albright (3). Such a value may be in error by as much as 10%, but the approximate value will often help simplify subsequent calculations.

(b) Determine a more exact SR value. The isomerization model can be used to predict partially hydrogenated products in a SR range covering ±15% of the approximate value. A plot can be made of (CC + CT) or of (C + T) versus IV at each SR value. The composition of the hydrogenated oil is then used with these plots to determine the exact SR value. An alternate and more sophisticated technique is to use a regression analysis to determine the exact SR value directly with the computer; Step a can then be eliminated altogether.

(c) Determine the II. Once the exact SR is determined, the model can be solved for II values in the range of SR to II from 2 to 15. Plots can be made of the *trans* acid content versus IV at the various II values. The *trans* content of the hydrogenated oil is then used to determine the II value. A regression technique can also be used with the computer to determine II directly. Steps a and c can be combined to determine both SR and II on the computer.

If a computer is not readily available at all times and if a given oil is to be hydrogenated for several runs, the isomerization model for the oil can first be solved for several SR values. SR values of 2,5,10,15,25,50 and 100 should in general be sufficient

TABLE I

Hydrogenation of Cottonseed Oil

IV	SR	% *Trans*	II	SR/II
76.2	1.4	6.9	0.28	5.0
60.7	1.7	9.8	0.30	5.7
49.8	2.0	10.6	0.30	6.7
81.4	2.7	9.5	0.59	4.6
70.5	2.4	12.0	0.53	4.5
59.3	2.8	14.9	0.55	5.1
48.1	3.2	15.0	0.47	6.8
81.8	6.0	22.6	1.6	3.7
65.3	6.0	29.1	1.6	3.7
53.7	7.2	29.5	1.4	5.5
70.0	10	29.8	1.7	5.9
56.2	10	32.4	1.5	6.7
44.4	10	31.6	1.6	6.2
77.7	26	26.8	4.4	5.9
73.6	22	28.6	3.8	5.8
81.0	30	22.8	4.0	7.5
72.3	28	29.4	4.0	7.0
76.6	46	26.3	4.5	10.2
64.7	46	35.1	4.5	10.2
75.8	50	26.5	4.4	11.4
69.7	58	30.9	4.2	13.8
77.6	18	31.4	8.7	2.1
70.1	17	36.7	7.6	2.2
77.2	20	33.9	11.3	1.8
69.8	26	39.0	9.4	2.8
76.9	45	31.0	10.0	4.5
71.1	45	37.2	11.0	4.1
76.3	80	30.8	10.5	7.6

TABLE II

Hydrogenations of Soybean Oil[a]

Temp., C	Pressure, psig	Catalyst	IV	SR	% *Trans*	II	SR/II
142	60	G-15	87.4	5.5	22.0	0.6	9
142	60	G-15	60.9	6	27.3	0.6	10
174	15	G-15	99.4	17	24.6	3.0	6
180	15	G-15	82.3	21	31.3	1.9	11
185	15	G-15	79.5	25	38.1	2.9	9
190	28	Nysel	108	7	19.6	3.1	2.2
164	17	Nysel	103	17	24.5	3.7	4.6
156	17	Nysel	95.4	20	28.1	2.7	7.5
166	39	Nysel	92.3	24	26.9	2.1	11
228	39	Nysel	102.2	40	27.9	4.4	9
220	17	Nysel	103.8	70	28.6	4.9	14

[a] Allen, personal communication.

to cover all ranges of selectivity of interest. At each SR value, several II values would be considered so that the ratio of SR to II would vary from about 2 to 15. Two types of plots could then be constructed: (a) diunsaturated acid content (CC + CT) versus IV with SR as the parameter, used to determine the exact SR value of the hydrogenated product, and (b) at a given SR value, *trans* acid content versus IV with II as the parameter, whereby several plots would have to be prepared because several SR values should be considered; the II value of the hydrogenated oil could be determined by an interpolation-extrapolation procedure using two or three plots in the approximate range of the actual SR value.

When soybean oil is considered, a modified two-step procedure is required because of the linolenic acid present in the starting oil. First a SR value is calculated using the model based on Equation 1 and using the integrated equations presented by Albright (3). Values of II are then determined by using CC′ and the model shown in Equation 6.

It should be emphasized that SR values for partial hydrogenations of soybean oil can not be calculated using CC′ values and Equation 6. That model predicts values for the monounsaturated groups that are too high because one triunsaturated group hydrogenates to 1.5 monounsaturated groups, and triunsaturates hydrogenate directly to monounsaturates. Although these reasons preclude use of the model for calculating SR values, the basic assumptions of the method seem reasonable for calculating II values for partial hydrogenations of soybean oils.

Results and Discussion

The geometrical isomerization model described here is applicable for partial hydrogenations of oils such as cottonseed, soybean and corn which are used for the manufacture of shortening and oleomargarine stocks. Being able to measure both selectivity and isomerization characteristics quantitatively will offer numerous advantages in describing the type of hydrogenation and also in tailoring desired products from given triglyceride feedstocks. These measurements will also be valuable in comparing catalysts. As has been suggested in the past (13), new hydrogenated products may be developed which have significantly different II values for a given SR as compared to presently available products. Modified nickel catalysts can in some cases be used to obtain such new products.

Both geometrical and positional isomerization involve the same chemical intermediates on the catalyst surface (6,7). The rate of total isomerization which includes both positional and geometrical isomerization is higher than that of just geometrical isomerization. Such a conclusion is obvious since some *cis* isomers are formed in addition to the *trans* isomers. As a result, the ratio of the rate of total isomerization to the rate of hydrogenation for either CC or C is greater than II. The above ratio would presumably vary between 1.0 and about 1.33. The upper limit for this ratio is set because up to one *cis* isomer can sometimes be formed for about every three *trans* isomers. In considering the initial oleic and linoleic acid groups though, some geometrical isomerization occurs without any positional isomerization. In the latter case, the ratio is 1.0. A higher ratio is expected as II increases. The value for II is thought however to be a semi-quantitative measure of positional isomerization.

The isomerization model can be considered at least semi-theoretical even though several empirical modifications are required in its use. Certainly better models can be developed in the future, but considerably more information is needed to obtain a completely theoretical model. In particular, information pertaining to the adsorption and desorption of families such as CT, T and C to and from the catalyst is needed. Since mass transfer resistances have such an important effect on the overall reaction scheme, it is recommended that additional information be obtained relative to the transfer steps to and from the catalyst.

REFERENCES

1. Albright, L. F., Chem. Eng. *1967,* 197.
2. Albright, L. F., JAOCS *40,* No. 5,16 (1963).
3. Albright, L. F., Ibid. *42,* 250 (1965).
4. Albright, L. F., M. M. Win and J. M. Woods, Ibid. *42,* 556 (1965).
5. Albright, L. F., and J. Wisniak, Ibid. *39,* 14 (1962).
6. Allen, R. R., and A. A. Kiess, Ibid. *32,* 400 (1955).
7. Allen, R. R., and A. A. Kiess, Ibid. *33,* 355 (1956).
8. Bailey, A. D., "Industrial Oil and Fat Products," 2nd Ed., Interscience, New York, 1951.
9. Eldib, I. A., and L. F. Albright, Ind. Eng. Chem. *49,* 825 (1957).
10. Feuge, R. O., M. B. Pepper, R. T. O'Connor and E. T. Field, JAOCS *28,* 420 (1951).
11. Litchfield, C., J. E. Lord, A. F. Isbell and R. Reiser, Ibid. *40,* 553 (1963).
12. Schmidt, H. J., Ibid. *45,* 520 (1968).
13. Stefanovic, S., and Albright, L. F., Ibid. *46,* 139 (1969).
14. Wisniak, J., and L. F. Albright, Ind. Eng. Chem. *53,* 375 (1961).

[Received February 24, 1970]