Quantitative Measure of Selectivity of Hydrogenation of Triglycerides

L. F. ALBRIGHT, Purdue University, Lafayette, Indiana

Abstract

Graphs have been prepared using a digital computer that allow the quantitative determination of the degree of selectivity for the hydrogenation of cottonseed, peanut, corn, soybean and linseed oils. Use of these graphs requires only a knowledge of the composition of the initial (unhydrogenated) oil and that of the hydrogenated oil plus simple calculations. If the exact composition of the initial oil is unknown, a typical composition can generally be assumed.

Introduction

THE NEED FOR AN easily applied, yet reliable, method for measuring quantitatively the degree of selectivity for the hydrogenation of common triglyceride oils and fats quickly becomes apparent to anyone studying the hydrogenation literature. Presently, hydrogenations are generally characterized as selective, very selective, moderately selective, moderately non-selective, etc. Such terms are obviously vague, and the hydrogenation that one person calls selective might very possibly be labeled differently by others. The present paper proposes a method for quantitatively measuring selectivity, and the easy steps required for using are explained.

The selectivity of the hydrogenation can be quantitatively measured as the ratio of the reactivities of the polyunsaturates to that of the monounsaturates. Since most unsaturated fatty acid groups in triglycerides commonly hydrogenated are C_{18} acids, the monounsaturated groups are generally designated as oleic acid groups, the diunsaturated groups as linoleic acid, and the triunsaturated groups as linolenic acid. Saturated acid groups, although they contain palmitic, myristic, etc. acids, are frequently called stearic acid.

In 1949, Bailey (3,4) demonstrated that the following model could be used to measure the relative reaction rate constants for each of the following hydrogenation steps occurring during the batch hydrogenation of linseed, soybean, and cottonseed oil:

$$\begin{tikzcd}
 & \text{linoleic} \arrow[dr] & & \\
\text{linolenic} \arrow[ur] \arrow[rr] \arrow[dr] & & \text{oleic} \arrow[r] & \text{stearic} \\
 & \text{isolinoleic} \arrow[ur] & &
\end{tikzcd} \qquad [A]$$

Using this model, he developed kinetic equations to represent the concn of each acid group as a function of time. Each reaction was assumed to be irreversible and first order. Since an induction period frequently occurs during hydrogenation, he used pseudo times in order to determine the reaction rate constants. The predicted results agreed within experimental accuracy of the data for several batch runs made at various operating conditions. Because pseudo times were employed, the reaction rate constants determined had to be designated as relative reaction rate constants. Bailey indicated that when the ratio (hereafter called the selectivity ratio) of the rate constant for linoleic acid to that for oleic acid was 31 or above, the hydrogenation was selective. Ratios of 7.5 or below were designated as non-selective hydrogenation. Ratios between 7.5 and 31 were not discussed by him, but they were apparently considered as in the intermediate range between selective and non-selective hydrogenations.

The chemical model as proposed by Bailey (3,4) does not indicate either positional or geometrical isomers that always occurs during hydrogenation. Positional isomers of monounsaturates in which the double bond has migrated along the fatty acid chain probably have relatively equal reactivities unless the double bond has migrated quite close to the ester group. When naturally occurring linoleic acid groups are hydrogenated, some conjugation of the double bonds occurs to produce a more easily hydrogenated material. It has been suggested that conjugation may occur in most, if not all, cases for linoleic acid before hydrogenation; however, this hypothesis has not been proved as yet. Isolinoleic acid (such as 9:10, 15:16 octadecadienoic acid) groups formed by the hydrogenation of the middle double bond of natural linolenic acid (9:10, 12:13, 15:16 octadecatrienoic acid) groups, however, have lower reactivties than natural linoleic acid groups (3,4). Regardless of the exact mechanism for the hydrogenation of linoleic acid, considering the linoleic acids as a single compound seems in general quite satisfactory. Obviously the rate constant determined with such an assumption is the average for all linoleic acid groups.

Geometrical isomers are not shown in the model proposed by Bailey (3,4). Albright and Wisniak (2) who used a more complicated reaction scheme involving both the *cis* and *trans* isomers of monounsaturated acid groups found that the reactivities of the geometrical isomers are comparable, if not identical, at hydrogenation conditions similar to those used commercially. Hence lumping the monounsaturates together, as Bailey did, is permissible in order to determine rate constants for measuring the degree of selectivity.

Bailey (3,4) first noted that *on a kinetic basis* linolenic acid sometimes hydrogenates directly to oleic acid. Scholfield et al. (8) later confirmed this finding. Albright and Wisniak (2) found that especially at very high pressures and high degrees of agitation linoleic acid appears to hydrogenate directly to stearic acid. The apparent hydrogenation of two double bonds simultaneously is rather easily explained. After the hydrogenation of one double bond, the partially hydrogenated acid group *at the catalyst surface* can do one of the following two things (1):

a) Remain at or near the catalyst surface until the second bond is hydrogenated. Simultaneous hydrogenation of both double bonds will then appear to have occurred, based on analyses of liquid in the main body of the oil.

b) Be transferred to the main body of the oil where it can be analyzed. Eventually this fatty acid group will be transferred back to the catalyst surface and be either hydrogenated or isomerized. In this case the double bonds will appear to hydrogenate by steps.

Ignoring the apparent simultaneous hydrogenation of two double bonds would not be serious in many cases, especially for oils containing little or no linolenic acid groups. Ignoring it would mean that the selectivity ratio (S.R.) would appear to change slightly as the hydrogenation progressed.

A complete set of reactions to represent each step in the hydrogenation of common triglycerides would be highly complicated. As has been discussed, several reasonable approximations can be made, and the following simplified set of reactions represents reasonably well in many cases the experimental data of batch hydrogenations at a given set of operating conditions:

$$\text{Linolenic} \rightarrow \text{Linoleic} \rightarrow \text{Oleic} \rightarrow \text{Stearic} \qquad [B]$$

The above set of reactions is also ideal for calculating the degree of selectivity of hydrogenation. In the final analysis, the composition of the hydrogenated product is the only criterion for measuring selectivity. The operating conditions for hydrogenation, of course, affect selectivity. Industrial batch hydrogenations, for example, are often made in which one or more of the operating variables, such as temp or pressure, vary during the run. Since the degree of selectivity depends on the operating conditions, selectivity in these cases varies during the run. The average degree of selectivity would, as a result, have to be determined from the final composition of the oil.

Application of Kinetic Equations

Kinetic equations for Model A, Model B or any other set of reasonable reactions can be applied only with considerable difficulty unless an analog or digital computer is used. Methods of using an analog computer have been discussed earlier (1,5).

Kinetic equations for Equations B, based on the assumptions of first order and irreversible reactions, are as follows:

$$1)\ \mathrm{Ll} = \mathrm{Ll_o}\, e^{-k_1 t}$$

$$2)\ \mathrm{L} = \mathrm{Ll_o}\left(\frac{k_1}{k_2 - k_1}\right)(e^{-k_1 t} - e^{-k_2 t}) + \mathrm{L_o}\, e^{-k_2 t}$$

$$3)\ \mathrm{Ol} = \mathrm{Ll_o}\left(\frac{k_1}{k_2 - k_1}\right)\left(\frac{k_2}{k_3 - k_1}\right)(e^{-k_1 t} - e^{-k_3 t}) - \mathrm{Ll_o}\left(\frac{k_1}{k_2 - k_1}\right)\left(\frac{k_2}{k_3 - k_2}\right)(e^{-k_2 t} - e^{-k_3 t}) + \mathrm{L_o}\left(\frac{k_2}{k_3 - k_2}\right)(e^{-k_2 t} - e^{-k_3 t}) + \mathrm{Ol_o}\, e^{-k_3 t}$$

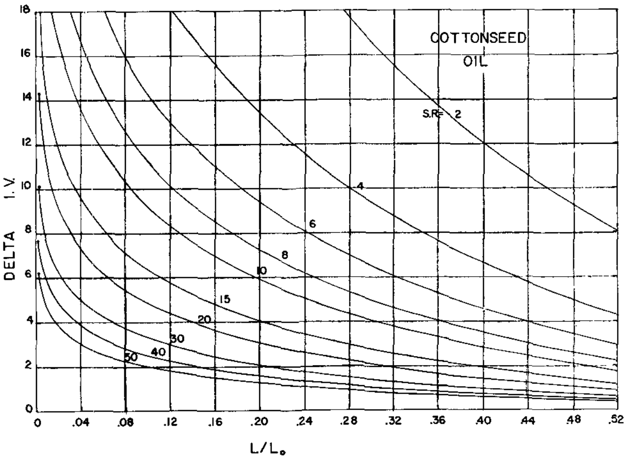

Fig. 1. Selectivity ratio (S.R.) for hydrogenated cottonseed oil.

where

Ll, L and Ol: the compositions on a mole percentage basis for the linolenic, linoleic and oleic acid groups respectively at time, t. (These compositions are on a 100% fatty acid basis; wt % can normally be substituted here since it is essentially identical to the mole %.)

$\mathrm{Ll_o}$, $\mathrm{L_o}$ and $\mathrm{Ol_o}$, the compositions of the linolenic, linoleic and oleic acid groups, respectively, of the initial oil.

t: time (pseudo time values were used here).

k_1: rate constant for the hydrogenation of linolenic acid to a linoleic acid.

k_2: rate constant for the hydrogenation of linoleic acid to an oleic acid.

k_3: rate constant for the hydrogenation of oleic acid to stearic acid.

These equations were programmed and solved using the IBM 7090 digital computer at Purdue University. Compositions employed for cottonseed, peanut, corn, soybean and linseed oils are shown in Table I. A total of at least 20 times values (actually pesudo time) from 0–6 or 8 were used; this range of times is sufficient to hydrogenate essentially all of the linolenic and linoleic acid groups in the oil. The k_2 value arbitrarily used in all cases was 1.0. k_1 was assumed to be 1.5, 2.0 and 2.5 which are in the range suggested earlier (3,4,8). Values of k_3 used were 0.020, 0.025, 0.0333, 0.04, 0.05, 0.0667, 0.1, 0.125, 0.1667, 0.25 and 0.5; hence ratios of k_2/k_3 defined as the selectivity ratio (S.R.) varied from 2–50, which is the range found as hydrogenation varies from highly non-selective to highly selective reactions.

TABLE I

Composition of Triglycerides Used in Computer Program

Oil	Type of oil	$\mathrm{Ll_o}$, % linolenic acid groups	$\mathrm{L_o}$, % linoleic acid groups	$\mathrm{Ol_o}$, % oleic acid groups
1	Cottonseed	....	59.7	14.9
2	Cottonseed	....	54.4	18.0
3	Cottonseed	....	36.8	30.0
4	Cottonseed	....	50.0	25.0
5	Peanut	....	26	57
6	Peanut	1.6	34	45
7	Peanut	1.5	18.5	66.5
8	Corn	....	50.0	40.0
9	Soybean	8.0	52.0	25.0
10	Linseed	54.0	17.0	21.0

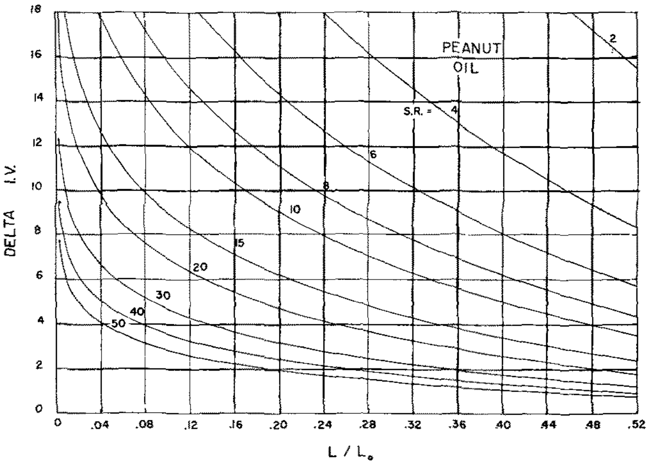

FIG. 2. Selectivity ratio (S.R.) for hydrogenated peanut oil.

The digital computer was also programmed with the following equations:

4) $S = 100.0 - Ll - L - Ol$
where S: the composition of the saturated acid groups, which includes stearic acid.

5) $I.V. = 2.6161\,Ll + 1.7321\,L + 0.8601\,Ol$
where I.V.: the iodine value of oil for a given Ll, L and Ol (on a % basis).

6) $R = L/L_0$
where R: the ratio of linoleic acid group that is unreacted.

7) $\Delta(I.V.) = 0.8601\,(Ll_0 + L_0 + Ol_0 - Ll - L - Ol)$.

Δ(I.V.) is the decrease of the iodine value that results in a given hydrogenation because of the non-selectivity of the reaction. With perfect selectivity, no stearic acid would be formed until all polyunsaturated acid groups were reduced to monounsaturates. The term, $Ll_0 + L_0 + Ol_0 - Ll - L - Ol$, then represents the amt of stearic acid that was formed because of the non-selective nature of the reaction. The term, Δ(I.V.), was used, as will be discussed later, in the final correlations.

The digital computer printed out for each calculation: time, k_2, Ll, L, Ol, S, I.V., R and Δ (I.V.).

Discussion of Computer Results

Selectivity can be measured quantitatively as the ratio of k_2/k_3, which is called the selectivity ratio (S.R.) for the hydrogenation. Calculations of S.R. for every oil hydrogenated even with a computer would be quite tedious; furthermore a computer is not always available. The computer results for the various oils shown in Table I were plotted at constant S.R. as the Δ(I.V.) versus L/L_0 (the fraction of linoleic acid unhydrogenated).

TABLE II

Comparison of the Calculated S.R. Values for (Cottonseed) Oils 1 and 3 with Predicted Values of Figure 1 (Oil 2)

Pseudo time	Calculated S.R. value	Predicted S.R. value	
		Oil 1	Oil 3
0.6	50	48	60
4.0	50	52	48
0.6	20	19	24
4.0	20	20	19
0.6	4	3.9	5.0
4.0	4	4.1	3.9

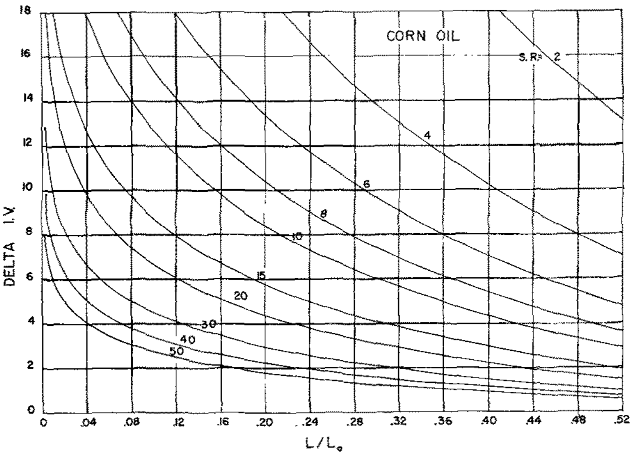

FIG. 3. Selectivity ratio (S.R.) for hydrogenated corn oil.

Figure 1 shows the results for (cottonseed) oil No. 2 (see Table I) which is a typical cottonseed oil. The S.R. values are higher at a given L/L_0 value when the Δ(I.V.) values are lower. All curves for given S.R. values approach Δ(I.V.) = 0 as L/L_0 approaches 1.0 (which is the condition for the unhydrogenated oil). As L/L_0 approaches zero, the values of Δ(I.V.) approach in all cases rather large numbers, especially at lower degrees of selectivity. The results for (cottonseed) oils No. 1 and No. 3 were compared to those of Figure 1, as shown in Table I. Oils No. 1 and No. 3 represent the extreme limits for the composition of cottonseed oils reported by O'Connor et al. (7). Values of S.R. for (cottonseed) oil No. 1 agree within 5% of the values of Figure 1. A slightly poorer agreement is found for oil No. 3 especially at lower times (which means less hydrogenation). The composition of oil No. 3 is quite different though than most other cottonseed oils. Oil No. 4 has a composition which is often used as an approx value for cottonseed oils. The computer results for this oil fit within 5% of the S.R. values of Figure 1. In general, it seems safe to conclude that Figure 1 will predict the S.R. values of most cottonseed oils to within 5%.

Figure 2 is the correlation of the computer results for (peanut) oil No. 5 which has a rather typical analyses for a peanut oil. The results for (peanut) oils No. 6 and No. 7 were compared to values in Figure 2 as shown in Table III. The calculation of the results for oils No. 6 and No. 7 is complicated somewhat by the linolenic acid present in the initial oil. The k_1 value was assumed to be 2.0. Latter calculations with soybean and linseed oils, which contain considerably more linolenic acid, indicated that the presence of the small amt of linolenic acid in the peanut oil had no significant effect on the calculations.

Table III indicates that Figure 2 predicts S.R. values for oil No. 6 that are in general ca. 5–10% low. On the other hand, the S.R. values for oil No. 7 are

TABLE III

Comparison of the Calculated S.R. Values for (Peanut) Oils 6 and 7 with Predicted Values of Figure 2 (Oil 5)

Pseudo time	Calculated S.R. value	Predicted S.R. value	
		Oil 6	Oil 7
0.6	50	43	55
4.0	50	47	55
0.6	20	18	23
4.0	20	19	22
0.6	4	3.6	4.7
4.0	4	3.8	4.4

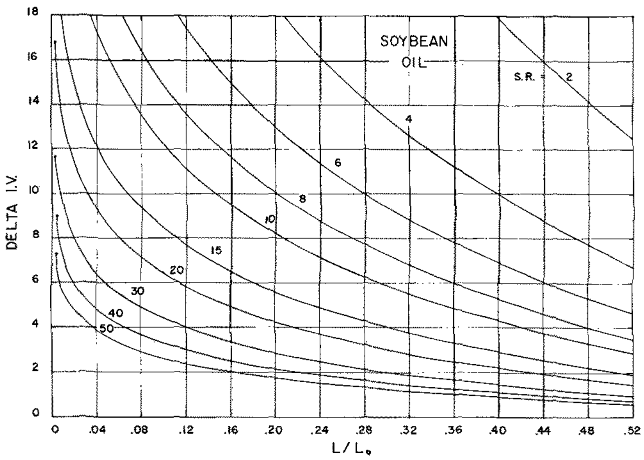

FIG. 4. Selectivity ratio (S.R.) for hydrogenated soybean oil.

generally 10–15% too high. The compositions of oils No. 6 and No. 7 are extremes in the list of peanut oils reported by French (6); his analytical results were converted to a 100% free fatty acid (FFA) basis. In general, Figure 2 should predict within ca. 10% the S.R. value of most peanut oils.

The correlations for (corn) oil No. 8 and for (soybean) oil No. 9 are shown in Figures 3 and 4, respectively. In both cases the compositions used are quite typical for the natural oils. Since soybean oil contains appreciable amt of linolenic acid groups (8% in the present example), the hydrogenation of linolenic acid is quite important. Values of k_1 employed were 1.5, 2.0 and 2.5; only small differences were noted in the three sets of results. The computer results for k_1 equals 2.0 were used in preparing Figure 4.

Figures 3 and 4 were, surprisingly, found to be almost identical; the S.R. agreed in all cases within ca. 5%. The S.R. curves for Figures 3 and 4 are essentially parallel to those of Figure 1 for cottonseed oil. Multiplying the S.R. of Figures 3 and 4 by 0.7 essentially duplicates the S.R. values of Figure 1. Figures 3 and 4 should be quite reliable for calculating S.R. for all hydrogenated corn and soybean oils, respectively.

For linseed oil, the major fatty acid component of the unhydrogenated oil is linolenic acid. During the initial stages of hydrogenation, the linoleic acid content increases until it reaches a maximum; then it decreases toward zero. Δ(I.V.) however increases during the entire reaction. Figure 5 is the correlation for (linseed) oil No. 10 plotted as Δ(I.V.) vs. the linoleic acid content for the final stages of the hydrogenation. Varying k_1 from 1.5–2.5, caused a variation of the S.R. of perhaps 10–15%. At higher degrees of selectivity (S.R. of 30 or above), 2.5 for k_1 would be preferred (3,4), but at lower selectivities (S.R. of 15 or less), 1.5 for k_1 is recommended. At intermediate degrees of selectivity, k_1 is probably ca. 2.0; interpolation between the curves for k_1 values of 1.5 and 2.5 is suggested. Since only one linseed oil was calculated and since linseed oil contains large quantities of linolenic acid (which is an added complication), Figure 5 is probably not as accurate for use with other linseed oils as Figures 1–4 are with their particular oils. It would be expected, however, that Figure 5 should be accurate to within at least 20% for most linseed oils, unless their compositions were very different than that of oil No. 10.

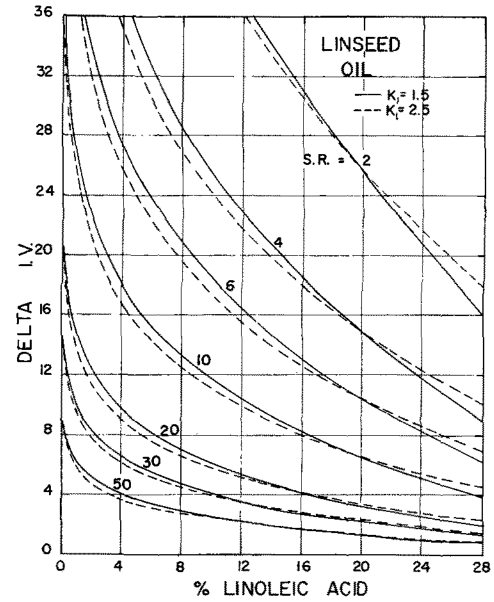

FIG. 5. Selectivity ratio (S.R.) for hydrogenated linseed oil.

Application of Graphs

Determination of the selectivity ratio (S.R.) for a hydrogenated oil using Figures 1–5 is easy and involves the following steps:

1) Determine the composition of the hydrogenated oil on a 100% FFA basis.
2) Determine the composition of the unhydrogenated oil. If the exact composition is unknown, it can probably be estimated with fair accuracy based on the composition of typical oils from the same source and with comparable history.
3) Calculate Δ(I.V.) using Equation 7.
4) Calculated the fraction of linoleic acid unreacted, i.e. L/L_0, if Figures 1, 2, 3 or 4 are to be used. With Figure 5, the linoleic acid content is the abscissa.
5) Using Δ(I.V.) and L/L_0 (or L in the case of Fig. 5), read the selectivity ratio off the appropriate graph (Figs. 1–5).

If future hydrogenation investigators will report the selectivity ratio (S.R.) of their reactions, the literature will be considerably clarified, and the degree of selectivity will be unequivocally known.

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