

Calculation of Catalyst Selectivity in Vegetable Oil Hydrogenation¹

C.R. SCHOLFIELD, R.O. BUTTERFIELD, and H.J. DUTTON, Northern Regional Research Center, Agricultural Research, Science and Education Administration, U.S. Department of Agriculture, Peoria, Illinois 61604

ABSTRACT

The description of catalysts in terms of the rates of reactions they promote is now feasible. Several procedures have been published in the literature for determining selectivity of hydrogenation catalysts, particularly as ratios of reaction rates. The present contribution reviews these procedures, tests their performance with sample data, and compares their merits.

INTRODUCTION

The knowledge that physical properties of a partially hydrogenated fat vary with conditions of reduction goes back to early use of the hydrogenation process. It was soon realized that the differences in physical properties were related to variations in fatty acid composition, and as early as 1917 Moore et al. (1) published results of a study of effect of conditions of hydrogenation on fatty acid composition of cottonseed oil. The concept of selectivity or preferential reduction of one kind of fatty acid over another seems to have begun in a qualitative way based on the properties of the product and to have included also the idea of amount of isooleic acid formation. As better methods for fatty acid analysis have developed, selectivity has come to refer to relative rates of hydrogenation of different fatty acids. Coenen (2) and Rozendaal (3) refer to four selectivity concepts: selectivities I and II, specific isomerization, and triglyceride selectivity. All affect properties of the hydrogenated oil, but here we are concerned only with the first two—referred to in this paper as linoleate selectivity, S_L , and linolenate selectivity, S_{Le} , and defined in the following paragraph.

In 1949, Bailey (4) proposed a reaction scheme for hydrogenation of oils and described the reactions by equations that were first order in fatty acid concentration. He also expressed selectivities as relative rates of reaction, ratios of rate constants of two fatty acids, so that time cancelled out and the ratios were independent of factors such as catalyst activity and overall rate of hydrogenation. Since then, most selectivities have been expressed in this way as ratios of rate constants of pseudo-first order reactions. Originally, most interest was in reaction rate of linoleate or of polyunsaturates with respect to oleate; but, with the great increase in soybean oil usage, the removal of linolenic acid has become of great interest, and we now speak of linoleate selectivity k_L/k_O and linolenate selectivity, k_{Le}/k_L (Le = linolenate, L = linoleate, O = oleate, S = saturate, k = rate constant).

Bailey, with data from Fisher et al., used a procedure of successive arithmetic approximations and trial and error to determine relative rates for the reactions of his scheme in several hydrogenations (4-6). Later, analog computers (7,8) were used to give more rapid solutions. More recently, digital computers (9) have been programmed to calculate solutions that best fit experimental data while eliminating the operator judgment involved in earlier methods. At our laboratory, a digital computer program, which we have called DRATE (9), has been developed, which by means of

different subroutines can be adapted to different and complex reaction schemes. A simplified form of DRATE called SELK (with keyboard printer input and printout) calculates linolenate and linoleate selectivity from initial and final composition for the simple $Le \rightarrow L \rightarrow O \rightarrow S$ consecutive reaction scheme (10). The program is written in Fortran IV and uses either card input and printer output or remote keyboard printer input and output.

An example of the remote keyboard printer format for the calculation of selectivity is shown in Figure 1, where the computer requests initial and final compositions, normalizes and prints them, and calculates a linolenate selectivity of 1.595 and linoleate selectivity of 33.63. As shown in Figure 1, total saturates are entered as part of the composition. Since only the 18 carbon acids are involved in the hydrogenation, the same selectivity values will be obtained using stearate instead of total saturates. When total saturates are used, the program also provides a calculated iodine value. However, the use of stearate instead of total saturates has the advantage of eliminating errors from analytical variations in palmitate between different gas chromatographic runs.

```
ENTER DATA TYPE-IN,HO,EX IDENT: 6A2 IN
ENTER TRIENE 8.77
ENTER DIENE 54.55
ENTER MONOENE 20.41
ENTER SATURATE 15.75

ENTER DATA TYPE-IN,HO,EX IDENT: 6A2 HO
ENTER TRIENE 5.22
ENTER DIENE 42.32
ENTER MONOENE 35.67
ENTER SATURATE 15.99

SAMPLE      TRIENE    DIENE    MONOENE  SATURATE  I.V.
INITIAL OIL  0.0882   0.5484   0.2052   0.1583    135.68
HYDROGENATED OIL 0.0526   0.4266   0.3596   0.1612    118.58

LINOLENATE SELECTIVITY 0.1595E+01
LINOLEATE SELECTIVITY  0.3363E+02
```

FIG. 1. An example of the remote keyboard printer format for SELK calculation of selectivity.

Other methods based on this simple consecutive reaction scheme have been described. Dutton (11) described a method for linolenate selectivity based upon the analysis for linolenate after absorption of 0.5 moles of hydrogen by an equal mixture of linoleate and linolenate. Okkerse et al. (12) presented equations for calculating linolenate selectivity. Their equations are based on the same assumptions and give the same selectivity values as our SELK computer method. Boelhouwer et al. (13) published curves illustrating hydrogenation of linoleic esters for different selectivities and corrected the curves for saturated acids in natural triglyceride oils. Useful graphical methods for linoleate selectivity have been published by Albright (14) and for linolenate selectivity by Allen (15).

The purpose of this paper is to compare the more elaborate DRATE method, which requires removal of samples at intervals as hydrogenation proceeds, with methods based only on initial and final composition and on the consecutive reaction model and to compare values by these various simpler methods among themselves.

¹Presented at the AOCS meeting, St. Louis, May 1978.

METHODS

Selectivities of Computer-Simulated Hydrogenations

Although the simple consecutive reaction scheme is used as a model in most selectivity calculations, it is generally agreed that a more complex model is necessary to represent an actual hydrogenation accurately. Bailey (4) included a pathway from linolenate through isolinoleate to oleate and a direct linolenate-to-oleate shunt. Other investigators have found similar models necessary. Selectivity calculations are further complicated in that gas chromatography, the common method of analysis, includes all diene isomers including isolinoleates in one diene fraction.

To obtain compositional data free from experimental variation, we simulated hydrogenations on a digital computer with reaction schemes as shown in Figure 2. Conditions were chosen based on Bailey's data and our own experience (16,17) to give what we believe are realistic values. Initial compositions are the same as those used by Albright (14). Hydrogenated sample compositions for soybean oil were read from the computer simulation at ca. 4, 2, 1, 0.5, and 0.2% linolenate as shown in Table I. These values are shown together with corresponding values for linoleate, isolinoleate, total diene, and selectivities. Similar values for linseed oil with linolenate values of ca. 40, 30, 20, 10, 5, 2, and 0.5% are in Table II. The simulated

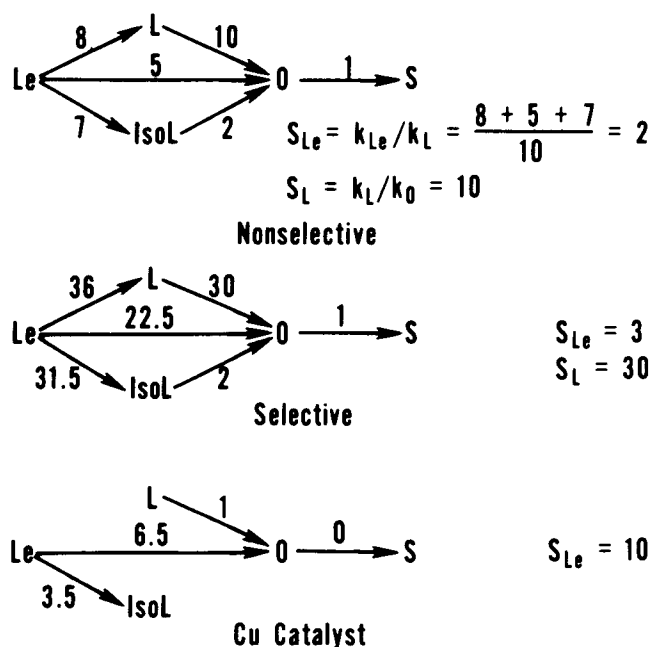


FIG. 2. Reaction schemes for simulated hydrogenation of 18 carbon acids to give compositions in Tables I and II.

TABLE I
Simulated Soybean Oil Hydrogenation for Reaction Schemes Shown in Figure 2

% Le	% L	% IsoL	% M	% S	S _{Le}		S _L	
					SELK ^a	Allen ^b	SELK ^a	Albright ^c
8.0	52.0	0.0	25.0	15.0				
Nonselective								
4.05	38.32	1.33	40.17	16.13	1.91	1.9	10.4	---
1.97	27.42	1.94	50.89	17.78	1.96	1.9	10.2	---
1.00	19.84	2.14	57.39	19.63	1.99	2.0	9.9	10
0.49	14.01	2.16	61.56	21.78	2.03	2.3	9.7	10
0.20	9.11	2.07	64.06	24.55	2.10	2.5	9.4	10
Selective								
4.26	43.48	1.30	35.74	15.21	2.79	2.7	33.8	---
2.07	34.97	2.04	45.38	15.54	2.88	2.9	31.4	---
1.01	27.88	2.37	52.80	15.94	2.95	3.0	30.3	---
0.49	22.12	2.52	58.49	16.38	3.02	3.3	29.5	29
0.20	16.48	2.57	63.75	17.00	3.09	3.3	28.7	29
Cu Catalyst								
3.97	48.48	1.41	31.31	15.00	5.84	6		
2.01	45.30	2.10	35.59	15.00	6.56	7		
1.08	42.57	2.42	38.92	15.00	7.11	7		
0.51	39.46	2.62	42.41	15.00	7.63	8		
0.20	35.99	2.73	46.08	15.00	8.19	8		

^aReference 10.
^bReference 15.
^cReference 14.

TABLE II
Simulated Selective Linseed Oil Hydrogenation for Selective Reaction Scheme Shown in Figure 2

% Le	% L	% IsoL	% M	% S	S _{Le}		S _L	
					SELK ^a	Allen ^b	SELK ^a	Albright ^c
54.00	17.00	0.0	21.00	8.00				
41.22	20.42	4.46	25.83	8.07	1.18	1.1	---	---
31.47	22.38	7.84	30.16	8.15	1.45	1.4	62.6	---
20.06	23.48	11.73	36.41	8.32	1.86	1.9	46.5	---
9.76	22.08	15.11	44.40	8.65	2.43	2.8	34.6	---
4.75	19.12	16.61	50.48	9.03	2.90	3.5	28.8	---
1.93	15.12	17.26	56.12	9.56	3.40	4.0	24.0	---
0.50	10.08	17.24	61.73	10.45	4.06	6.0	19.8	20

^aReference 10.
^bReference 15.
^cReference 14.

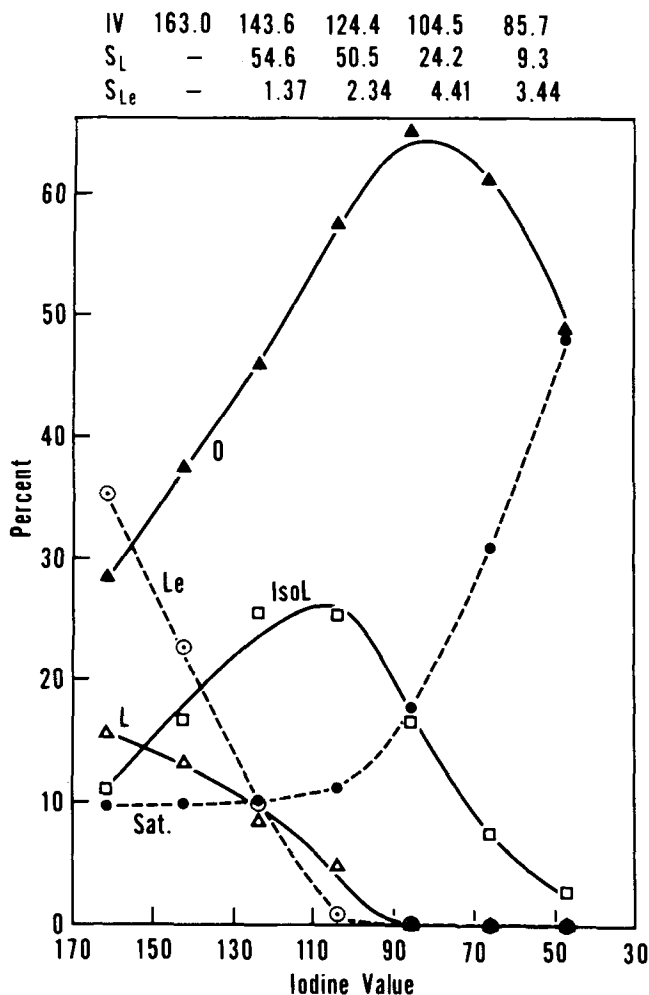


FIG. 3. Selective hydrogenation of linseed oil (Bailey's data). Percent composition vs. iodine value with SELK selectivities (4,10).

compositions have been listed to two decimal places. Although such accuracy is not obtained experimentally by gas chromatography, the extra significant figures are useful for illustrating trends in selectivity values and may be of value to others needing simulated data. Selectivities are calculated from the composition of the initial oil and that of each hydrogenated sample. Linoleate and isolinoleate are combined as would occur with data from an actual gas chromatographic analysis. As would be expected with increasing isolinoleate formation, linoleate selectivity decreases and linolenate selectivity increases with increasing degree of hydrogenation. Variations are small with soybean oil, but because of the larger initial linolenate they are much larger with linseed oil. If linseed oil, for example, were hydrogenated to secure larger linolenate values for greater analytical accuracy, it would be necessary to specify the extent of hydrogenation. Values in ranges which can be read off Albright's (14) and Allen's (15) curves agree well with SELK computer values, but Allen's linolenate selectivity tends to become slightly larger as hydrogenation proceeds.

Selectivities Calculated from Experimental Data

Published sets of hydrogenation data suitable for DRATE simulations, where a number of samples have been withdrawn and analyzed, are limited. Those used by Bailey (5,6) are among the most complete. Although some of the analytical methods are out of date, his data sets give error terms in DRATE calculations of similar values to those obtained with more recent data and appear to be of comparable accuracy. For his cottonseed oil data, a consecutive

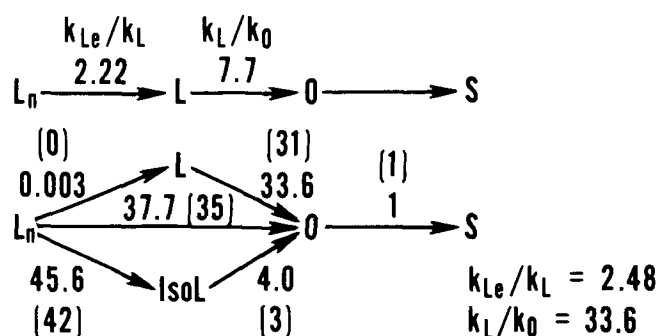


FIG. 4. Selective hydrogenation of linseed oil (Bailey's data). DRATE values of relative rates compared with Bailey's values in parentheses (4,9).

reaction DRATE calculation gave linoleate selectivity of 37 compared to his value of 38. SELK calculations gave values from 77 to 29, generally decreasing as the hydrogenation proceeded but with some scatter probably caused by analytical errors. Albright's graphical method agreed well with SELK values.

Bailey's soybean data did not give a good fit in DRATE calculations, and SELK values were erratic but his linseed data gave good DRATE fits. Figure 3 shows a DRATE computer fit to his selective linseed oil hydrogenation data with SELK values at the top. Figure 4 compares the DRATE relative rates with his values shown in parentheses. Similar results were obtained with the nonselective hydrogenation. Relative rates which are similar to Bailey's and SELK values confirm the trends found in the simulated hydrogenation and illustrate the importance of multiple pathways.

As examples of other hydrogenations, Figure 5 is based on data published by a commercial catalyst company (18) for nickel hydrogenation of soybean oil. Figure 6 shows a copper-catalyzed hydrogenation of soybean oil. The data (Friedrich, J.P., and T.L. Mounts, Private Communication) were obtained during work on high pressure, copper-catalyzed hydrogenation by the method previously described (19).

Selectivities are somewhat more erratic than for simulated hydrogenations due at least in part to analytical variation in the compositions. In Figure 5, linolenate selectivity increases with extent of hydrogenation, but the expected decrease in linoleate selectivity found in the simulated hydrogenations is not evident. In Figure 6, linolenate selectivity increases as expected. Possibly because small amounts of linolenate measured by alkali isomerization are more reproducible, all the linolenate selectivity values are reasonable.

DISCUSSION AND CONCLUSIONS

The examples presented here agree with our knowledge that hydrogenation of oils is much more complex than represented by the $Le \rightarrow L \rightarrow O \rightarrow S$ consecutive reaction scheme. If it is desired to consider the reaction mechanism or characterize the behavior of the catalyst in detail, analysis of a number of samples and application of a more complex model is necessary. For this, computer solutions with a program such as our DRATE is needed. Even if only a single selectivity value is desired, a DRATE computer solution of the consecutive reaction scheme with intermediate samples compensates for error in individual analyses and gives more reproducible results. However, many times these intermediate samples required for DRATE are not available. Also, in commercial hydrogenation, it is the final product which is of concern, and intermediate compositions are of lesser importance. Here, methods based on

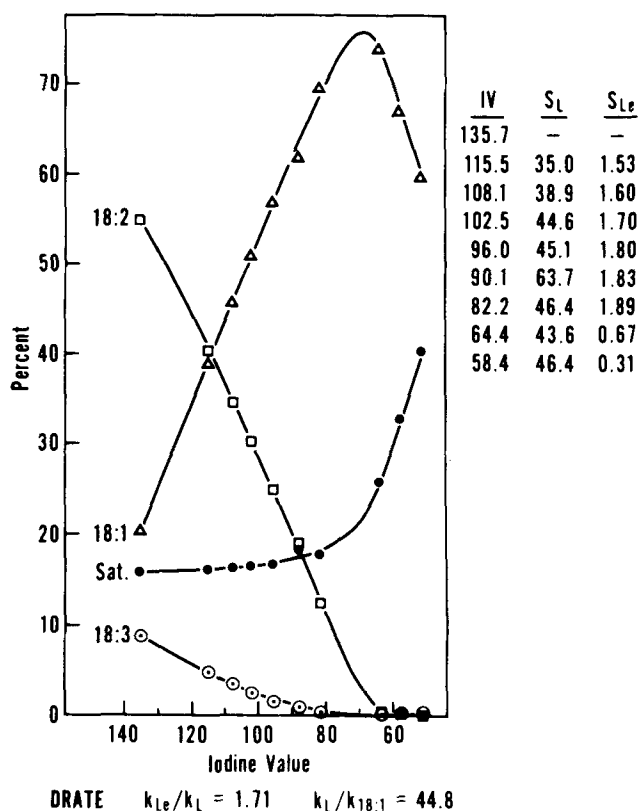


FIG. 5. Hydrogenation of soybean oil. Ni Catalyst, 200 C, 3 atm, with SELK and DRATE values (9,10,18).

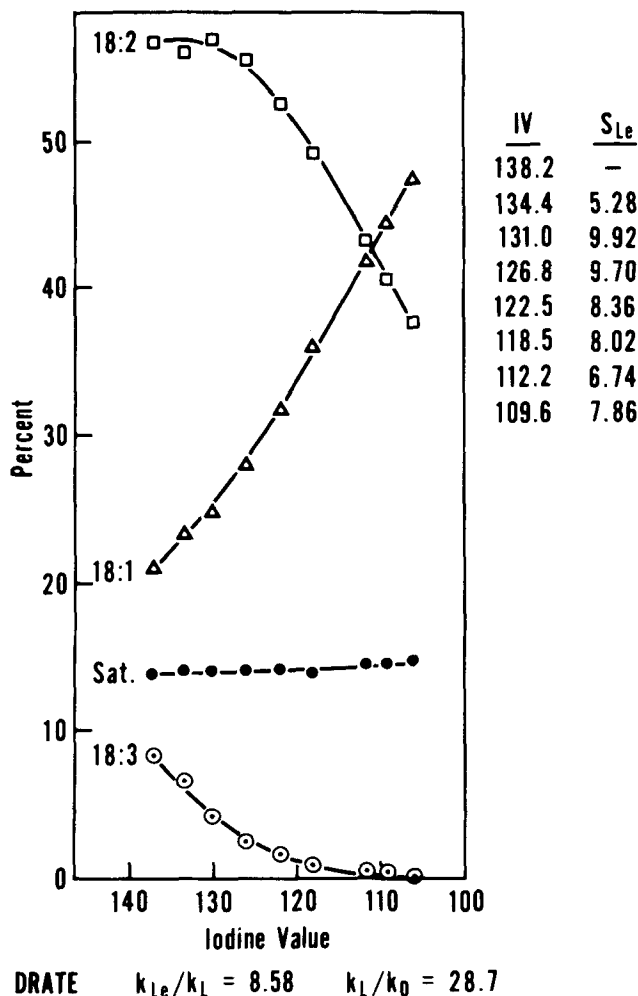


FIG. 6. Hydrogenation of soybean oil. Cu Catalyst, 150 C, 4000 psi, with SELK and DRATE values (9,10). Linolenate determined by alkali isomerization.

initial and final composition are of great value; but, for greatest reproducibility, the extent of hydrogenation needs to be specified especially when linolenate is present. Also, one should be aware of the extent to which selectivity values based on single samples may be affected by analytical error. A computer program like our SELK provides a convenient, rapid method of the widest applicability. The same linolenate selectivity can be obtained from the Okkerse et al. (12) equations by a trial-and-error solution. Values by the Albright (14) and Allen (15) graphical methods are comparable to our SELK computer values. Although for certain compositions values cannot be read on the graphs, they afford simple methods for those ranges represented by commercial products and most suited for characterization of catalyst.

REFERENCES

- Moore, H.K., G.A. Richter, and W.B. Van Arsdel, *Ind. Eng. Chem.* 9:451 (1917).
- Coenen, J.W.E., *JAOCS* 53:382 (1976).
- Rozendaal, A., International Society for Fat Research, Proceedings of the 13th World Congress, Paris Symposium 1, p. 43. (1976).
- Bailey, A.E., *JAOCS* 26:644 (1949).
- Bailey, A.E., and G.S. Fisher, *Ibid.* 23:14 (1946).
- Fisher, G.S., R.T. O'Connor, and F.G. Dollear, *Ibid.* 24:382 (1947).

- Butterfield, R.O., E.D. Bitner, C.R. Scholfield, and H.J. Dutton, *Ibid.* 41:29 (1964).
- Albright, L.F., and J. Wisniak, *Ibid.* 39:14 (1962).
- Butterfield, R.O., *Ibid.* 46:429 (1969).
- Butterfield, R.O., and H.J. Dutton, *Ibid.* 44:549 (1967).
- Dutton, H.J., *Ibid.* 39:95 (1962).
- Okkerse, C., A. DeJonge, J.W.E. Coene, and A. Rozendaal, *Ibid.* 44:152 (1967).
- Beolhouwer, C., J. Snelderwaard, and H.I. Waterman, *Ibid.* 33:143 (1956).
- Albright, L.F., *Ibid.* 42:250 (1965).
- Allen, R.R., *Ibid.* 44:466 (1967).
- Scholfield, C.R., J. Nowakowska, and H.J. Dutton, *Ibid.* 39:90 (1962).
- Vigeron, P.Y., S. Koritala, R.O. Butterfield, and H.J. Dutton, *Ibid.* 49:371 (1972).
- Nysel DM3 test results on soybean oil, The Harshaw Chemical Company.
- Mounts, T.L., S. Koritala, J.P. Friedrich, and H.J. Dutton, *JAOCS* 55:402 (1978).

[Received October 30, 1978]