Laboratory-Scale Continuous Hydrogenation: Copper Catalysis

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ABSTRACT

Soybean oil was partially hydrogenated with copper catalyst in an isothermal, concurrent, flow type reactor to reduce linolenate content. Reaction proceeded at one atmosphere outlet pressure; the parameters of temperature, catalyst concentration and oil flow rate (residence time) were varied. The reactor was designed to permit sampling at points along its length. Intermediate and final samples were analyzed to give total characterization of the partially hydrogenated oil. Data thus obtained were used to model and simulate the continuous hydrogenation kinetics. Linolenate selectivity is high and variations in reaction parameters appeared to have little effect. Specific isomerization values were increased as catalyst concentration increased but were unaffected by temperature and oil flow rate. Conjugated diene formation went through a maximum as the hydrogenation proceeded. Results of the copper-catalyzed continuous hydrogenations were compared to those of batch hydrogenations using the same reaction parameters.

INTRODUCTION

We have previously characterized the nickel-catalyzed, partial hydrogenation of soybean oil in a continuous flow reactor (1). Soybean oil has been hydrogenated in continuous systems using fixed beds of copper-based catalysts (2) and suspensions of oil and catalyst (3,4). Unreduced linolenic acid was greater than in batch hydrogenations, and the linolenic acid selectivity did not approach the values reported in batch reactions (5). Copper hydrogenated soybean salad oils have higher polyunsaturated fatty acid contents and greater yields of finished oil relative to nickel-hydrogenated soybean oils (6). However, commercial implementation of copper catalysis has been slow due in part to the low activity of copper catalysts and susceptibility of the catalyst to poisons. Both laboratory and plant experience indicates that removal of copper is not a problem in the use of this catalyst (7). Post-bleaching with activated earth has been shown to effectively remove the hydrogenation catalyst. It may be that continuous systems offer the best opportunity for the application of copper catalysis to the hydrogenation of soybean oil. The present paper reports the results of the light hydrogenation of soybean oil using a suspended copper-based catalyst in the laboratory-scale continuous reactor.

EXPERIMENTAL PROCEDURES

Refined and bleached soybean oil [Iodine Value (IV) = 137] was used for all hydrogenations. The catalyst was Harshaw Experimental Copper Chromite Catalyst 447A-26-3-21, which contains 38.6% CuO, 32.2% Cr_2O_3, and 1.42% MnO.

Hydrogenations were carried out in a pipe line reactor that was similar to one described previously (1). The apparatus was modified by increasing the length to 20 m of 0.12 cm I.D. Teflon tubing with six sampling outlets spaced at equal distances along the reactor. Oil and hydrogen were metered concurrently through the premixer described previously (1) into the reactor. Oil flow rate and hydrogen flow rate were measured at the end of the reactor. All hydrogenations were run at one atmosphere outlet pressure.

A central composite experimental design was used to obtain a statistical analysis of the hydrogenations (8). This design incorporates a series of reactions wherein all parameters are held constant to provide a measure of the reproducibility of the reaction. Operating conditions for these experiments included temperatures ranging from 175 C to 215 C; oil flow rate varied from 1 ml/min to 5 ml/min with the residence times of oil in the reactor ranging from ca. 2 to 7 min; and catalyst concentration varied from 3-7% weight of oil. The hydrogen flow rate was maintained at 300 ml/min. As reported previously with nickel, when operating at high gas velocities reaction data were not affected by the hydrogen flow rate (1).

Batch hydrogenations at atmospheric pressure were carried out in a manometric reactor (9). Temperature and

TABLE I

Reproducibility of Reactions
(195 C; 5% CuCr catalyst; oil flow rate – 2 ml/min)

	Fatty acid composition								
Run number	Saturate (%)	Monoene (%)	Diene (%)	Conjugated diene[a] (%)	Triene[b] (%)	ΔIV[c]	*trans* (%)	S_i[d]	S_{II}[e]
1	14.7	38.3	43.4	3.2	0.4	22	12.7	0.58	15.6
2	14.1	38.2	43.8	3.5	0.4	21	12.3	0.58	16.3
3	14.0	38.0	44.0	3.5	0.5	21	11.8	0.56	14.8
4	14.0	35.9	45.8	3.7	0.6	19	10.9	0.57	16.0
5	14.8	37.5	44.1	3.2	0.4	22	12.5	0.57	15.5
6	14.3	37.1	44.7	3.3	0.6	20	11.7	0.58	13.3
Standard deviation	0.32	0.83	0.77	0.18	0.09	1.1	0.60	0.007	0.99

[a] Determined by ultraviolet absorption.
[b] Determined by alkali isomerization.
[c] ΔIV – Change in iodine value.
[d] Specific isomerization – % *trans*/ΔIV.
[e] Linolenate selectivity (calculated from computer simulation data).

TABLE II

Continuous Hydrogenation of SBO-CuCr

Conditions			Fatty acid composition								
Temp. (C)	Oil flow (ml/min)	Cat. conc. (%)	Saturate (%)	Monoene (%)	Diene (%)	Conjugated diene[a] (%)	Triene[b] (%)	ΔIV[c]	S_i[d]	S_{II}[e]	ΔIV/min
Original oil			13.9	22.2	55.5		8.4				
185	2	4	14.3	35.2	46.3	3.7	0.5	19	0.52	16.4	3.2
195	2	4	14.8	37.0	44.8	3.1	0.3	21	0.54	15.5	3.5
205	2	4	13.9	44.3	39.2	2.4	0.2	27	0.54	14.5	4.5
185	2	6	14.9	37.7	43.9	2.9	0.6	22	0.57	13.4	3.3
195	2	6	14.7	40.8	41.0	2.9	0.6	24	0.60	9.3	4.0
205	2	6	14.3	46.5	37.1	2.0	0.1	29	0.60	13.0	4.8
185	4	4	14.5	22.4	54.7	1.2	7.2	3	0.54	18.8	0.8
205	4	4	14.5	24.4	52.4	4.9	3.8	7	0.57	13.9	1.8
185	4	6	14.2	31.1	48.7	4.4	1.6	14	0.58	12.8	3.5
205	4	6	13.9	32.5	48.2	4.2	1.2	15	0.61	15.0	3.8
195	1	5	15.1	52.0	30.7	1.7	0.5	35	0.59	8.4	4.4
195	2	5	15.2	48.3	34.9	1.2	0.4	32	0.57	10.0	4.5
195	4	5	14.6	33.5	46.7	4.0	1.2	17	0.57	8.7	4.3
195	5	5	14.2	29.4	49.3	4.6	2.5	12	0.58	13.0	4.0
195	3	3	14.5	28.7	50.8	4.3	1.7	13	0.53	18.2	2.6
195	3	7	14.3	39.7	42.7	2.9	0.4	23	0.62	13.4	4.7
175	3	5	14.1	24.4	53.2	3.1	5.2	3	0.56	13.1	1.0
215	3	5	14.4	44.0	38.7	2.5	0.4	27	0.56	15.0	5.4

[a] Determined by ultraviolet absorption.
[b] Determined by alkali isomerization.
[c] ΔIV – Change in iodine value.
[d] Specific isomerization – % *trans*/ΔIV.
[e] Linolenate selectivity (calculated from computer simulation data).

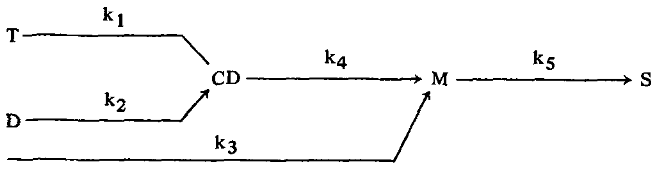
catalyst concentration were the same as used for the continuous reactor to facilitate comparisons of results.

Methyl esters of the partially reduced samples were prepared by transesterification of the oil with sodium methoxide catalyst (10) in methanol. Methyl esters were analyzed with a Varian Aerograph gas chromatograph (GC) operated isothermally at 185 C (separatory column: 6 ft x ¼ in. aluminum column packed with 10% EGSS-X, Applied Science Laboratory). The percent isolated *trans* was measured using AOCS Official Method Cd-14-61 (11). Percent linolenate was determined by alkali isomerization, and diene conjugation was determined by ultraviolet absorption using AOCS Official Method Cd-7-58 (11). Fatty acid composition and the iodine value of the reduced samples were computed from the GC and spectrometric data. High performance liquid chromatography was used to separate the *cis*-monoene, *trans*-monoene, and diene fractions (12). The double bond distribution in the monoene and diene fractions was determined from the sodium borohydride-reduced ozonides (13).

RESULTS AND DISCUSSION

Data for the final samples obtained in these reactions where all parameters are held constant (Table I) and similar results reported in our previous study (1) demonstrated the reproducibility of the laboratory-scale continuous reactor.

In fitting experimental compositions to a model to calculate relative reaction rates (14), the simple consecutive reaction scheme Triene→Diene→Monoene→Saturate used with nickel (1) did not give a good fit with the copper-catalyzed hydrogenations described here. The following model gave small error terms and was used, although with copper catalysts all diene actually is reduced through a conjugated diene intermediate (CD).



Therefore, linolenate selectivity (S_{II}) was calculated as $S_{II} = k_1/(k_2+k_3)$.

The continuous hydrogenation results are tabulated in Table II. The lower activity of the copper catalyst compared to the nickel catalyst used previously (1) required that the reactor in this study be lengthened to increase the residence time and that the amount of catalyst be greater. The rate of hydrogenation (ΔIV/min) was significantly increased by increase in temperature and/or catalyst concentration. S_{II} did vary due to experimental error, but was high and was not statistically influenced by variations in the parameters studied.

Koritala and Dutton found in batch hydrogenation of soybean oil with copper catalyst that linolenic acid and linoleic acid are reduced through a conjugation mechanism (5). In all copper-catalyzed hydrogenations except those at much higher pressures, conjugated diene has been determined as a measurable product. At the lower pressures used here, the conjugated intermediates tend to desorb from the

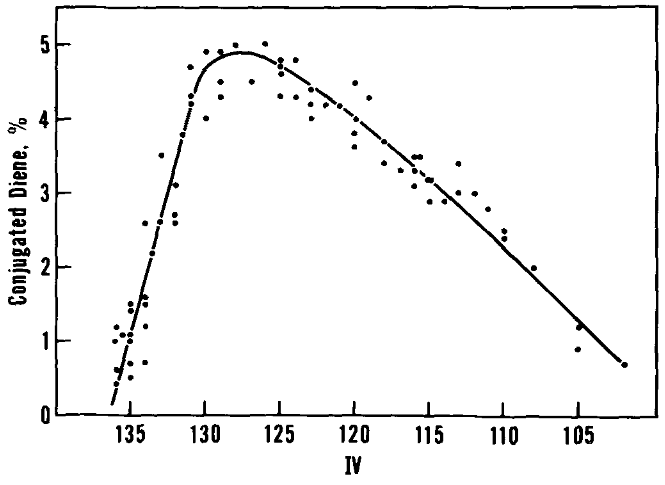


FIG. 1. Conjugated diene vs. iodine value. All samples removed from each hydrogenation are included.

TABLE III

Comparison of Batch and Continuous Reactors

Type of reactor	Temperature (C)	Cat. conc. (%)	ΔIV[a]	ΔIV/min	S_i[b]	Conjugated diene[c] (%)	Triene[d] (%)	S_{II}[e]
Continuous	185	4	19	3.2	0.52	3.7	0.5	16.4
Batch	185	4	19	1.5	0.52	5.2	1.0	10.8
Continuous	185	6	15	3.8	0.58	4.4	1.6	12.8
Batch	185	6	17	1.7	0.59	5.8	1.4	8.6
Continuous	205	4	27	4.5	0.54	2.4	0.2	14.5
Batch	205	4	21	2.0	0.52	5.4	0.9	9.9
Continuous	205	6	29	4.8	0.60	2.0	0.1	13.0
Batch	205	6	25	2.3	0.58	4.6	0.7	7.1

[a] ΔIV-Change in iodine value.
[b] Specific isomerization – % *trans*/ΔIV.
[c] Determined by ultraviolet absorption.
[d] Determined by alkali isomerization.
[e] Linolenate selectivity (calculated from computer simulation data).

catalyst before reduction and to appear in the product. The conjugated diene formed is plotted vs. the iodine value (Fig. 1) and shows that there is a maximum amount of conjugated diene present when the iodine value is about 130.

trans Isomer content (Fig. 2) tended to increase linearly with a decrease in iodine value (7,15,16). Formation of *trans* isomers increased slightly with an increase in catalyst concentration. Specific isomerization values (S_i), percent *trans* formed per unit iodine value drop, were 0.52 with 3-4% catalyst and 0.60 with 6-7% catalyst concentration.

Results of batch and continuous reactions performed at the same conditions are compared in Table III. In each comparative reaction, the rate of hydrogenation (ΔIV/min) was significantly lower when performed as a batch operation. This observation is in agreement with the findings of Ilsemann and Mukherjee (4), who previously reported high speed hydrogenations of oils in continuous reactors. The S_{II} determined for these comparative reactions showed that selectivity was significantly higher when operating in a continuous mode. It should be noted that batch hydrogenations using copper chromite catalysts have been performed previously at pressures above atmospheric (5,15); S_{II} was found to be much higher than the values determined here for reactions at atmospheric pressure.

Geometric isomerization tended to be much the same for both type of reactors; catalyst concentration again increased the amount of *trans* formed.

The diene fractions from both types of reactors were analyzed for positional isomerization. Double bonds were located in the 9 and 12 positions, which indicated that linolenate was reduced directly through the conjugated mechanism since no nonconjugated linoleate isomers were produced.

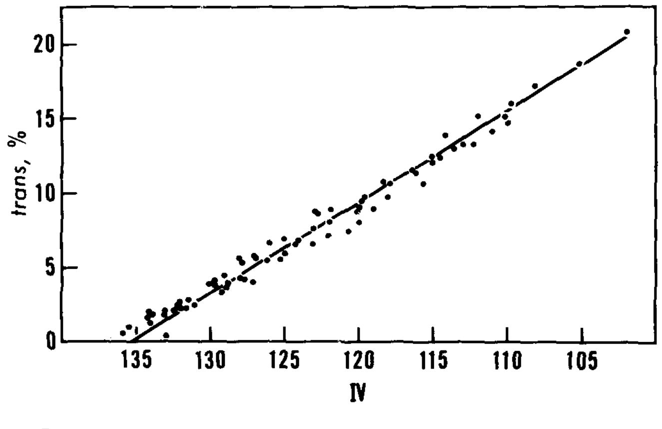


FIG. 2. *trans*-Isomers vs. iodine value. All samples removed from each hydrogenation are included.

Positional isomer analysis for the monoene fractions isolated from the oils hydrogenated in the batch and continuous reactions at 205 C is presented in Figure 3. *cis*-Monoene fractions from continuously reduced oils consisted mainly of the Δ9 isomer, with small amounts of Δ8, Δ10, Δ11, and Δ12 isomers. The Δ10 and Δ11 isomers were present in larger amounts of the *trans*-monoene, with a spread of other isomers from Δ7 to Δ15. A comparison of the isomeric distribution, both in the *cis* and *trans* fractions, indicates that the continuous reaction produced less isomerization than the batch reaction.

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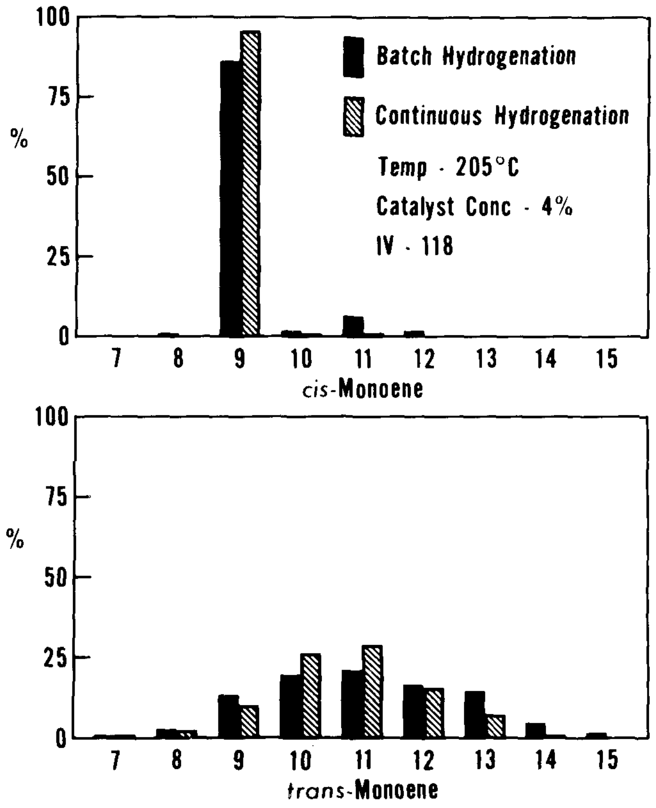

FIG. 3. Double bond distribution of *cis* and *trans* monoenes from both types of reactors.

REFERENCES

1. Snyder, J.M., H.J. Dutton, and C.R. Scholfield, JAOCS 55:383 (1978).
2. Mukherjee, K.D., I. Kiewitt, and M. Kiewitt, Ibid. 52:282 (1975).
3. Schmidt, H.J., Ibid. 47:134 (1970).
4. Ilsemann, K., and K.D. Mukherjee, Proceedings 13th World Congress, ISF Symposium 1 1977, p. 85.
5. Koritala, S., and H.J. Dutton, JAOCS 43:556 (1966).
6. Cowan, J.C., S. Koritala, K. Warner, G.R. List, K.J. Moulton, and C.D. Evans, Ibid. 50:132 (1973).
7. List, G.R., C.D. Evans, R.E. Beal, L.T. Black, K.J. Moulton, and J.C. Cowan, Ibid. 51:239 (1974).
8. Cochran, W.G., and G.M. Cox, Experimental Designs— 2nd Edition, 349 (1964).
9. Johnston, A.E., D. Macmillan, and H.J. Dutton, JAOCS 39:273 (1962).
10. Christopherson, S.W., and R.L. Glass, J. Dairy Sci. 52:1289 (1969).
11. AOCS, "Official and Tentative Methods of the American Oil Chemists' Society," Second Edition, AOCS, Champaign, IL, 1964.
12. Scholfield, C.R., Anal. Chem. 47:1417 (1975).
13. Johnston, A.E., H.J. Dutton, C.R. Scholfield, and R.O. Butterfield, JAOCS 55:486 (1978).
14. Butterfield, R.O., Ibid. 46:429 (1969).
15. Mounts, T.L., S. Koritala, J.P. Friedrich, and H.J. Dutton, Ibid. 55:402 (1978).
16. Moulton, K.J., R.E. Beal, and E.L. Griffin, Jr., Ibid. 48:499 (1971).

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