Laboratory-Scale Continuous Hydrogenation[1]

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ABSTRACT

Data required for modeling and simulation of continuous hydrogenation kinetics have been obtained in an isothernal, cocurrent flow-type reactor. A preheated suspension of catalyst in oil, mixed with hydrogen, is passed cocurrently through 10 m length of 0.12 cm ID Teflon tubing at flow rates varying from 1.5 to 4.5 ml/min, gas flow rates from 100 to 700 ml/min, and temperatures from 150 to 190 C. The hydrogenations are run using nickel catalyst at outlet pressures of one atmosphere. Samples are removed at equal intervals along the length of the reactor and analyzed by gas chromatography. The kinetics of the continuous reactor are satisfactorily modeled by the simple scheme Ln → Lo → 01 → S using first order kinetics. Reaction rates, calculated by a digital computer, are shown to be related to temperature by the Arrhenius equation. *trans* Content and degree of hydrogenation are increased with temperature are decreased as oil flow increases. Hydrogen flow rate has little or no effect over the range studied.

INTRODUCTION

Hydrogenation is the only unit operation in the processing of edible oils that is still largely performed as a batch process. However, it was suggested in 1967 (1) that a plant processing 100 million pounds of products per year might save 0.04 to 0.06 cents per lb by continous rather than batch hydrogenation. Many continuous processes have been proposed (2-4), but continuous hydrogenation has been slow to replace the well-established batch process. To be widely used, a continuous process should minimize backmixing and be capable of highly selective reduction of linolenic acid; it should be amenable to automated control to make uniform products, and it should have low hold-up to facilitate change from one product to another.

Continuous flow processes generally have different operating conditions than batch reactors including different mixing characteristics and shorter residence times. Several investigations have been made studying the effects of various operating conditions on the products formed (4-6). This paper presents results of additional studies with a small laboratory-scale continuous reactor.

EXPERIMENTAL PROCEDURES

Refined and bleached soybean oil was used throughout the study. The percent fatty acid composition determined by gas chromatography was: 16:0, 10.7; 18:0, 4.2; 18:1, 23.7; 18:2, 53.7; 18:3, 7.7. The iodine value was 133.5. Girdler G-15 nickel catalyst was used at a level equivalent to 0.3% nickel.

Reduction of the soybean oil was accomplished in a pipe type reactor. To increase dispersion of hydrogen into the oil, this laboratory-scale apparatus included a premixer constructed of a column 20-cm long, 0.22 cm ID containing a static mixer of 20 fixed helical elements (7). These elements were positioned in a way that the edge of one was 90° to the edge of the next element. The premixer was followed by a 10-meter length of 0.12 cm ID Teflon tubing reactor. The coiled tubing was heated in a constant temperature oil bath. Oil-catalyst suspension was metered into the premixer concurrently with a turbulent flow of hydrogen through a 27-gauge needle. Hydrogen was supplied from a gas cylinder at 10-20 psig. The oil flow and hydrogen flow rates were measured at the outlet at one atmosphere pressure. Teflon tees were placed at three equidistant points located in the reactor section for withdrawing 0.2-ml samples through a valve into a syringe. These samples of oil and catalyst were removed after the hydrogenation reached a steady state with a minimum time of 4 min between samples. A sample was collected from each of the three positions, and a fourth sample was collected at the outlet. Temperature also was monitored in the reactor by inserting thermocouples at the sampling positions.

In order to verify that there was minimal backmixing and to determine residence time, a dye was injected into the system prior to the premixer. The effluent was monitored by a Cary Recording Spectrophotometer in the visible range at the maximum absorption of the dye; as shown in Figure 1, the indication was that the dye eluted through the reactor with no backmixing. This appeared to show that at the high flow rate of hydrogen, there was turbulent action in the reaction tube.

The experimental design for the hydrogenations was a central composite design with three independent variables—temperature, oil flow rate, and hydrogen flow rate (8). A total of 20 hydrogenations were carried out. Temperature levels for the hydrogenations varied from 150 to 190 C. Oil flow rates were tested at three levels from 2 to 4 ml/min and hydrogen flow from 100 to 700 ml/min. The effect of these

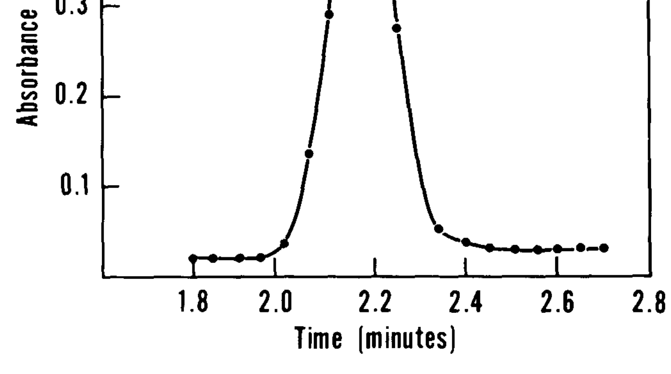

FIG. 1. Elution of dye in passage through reaction vessel. Time is measured from start of injection. Reaction conditions: temperature – 160 C; oil flow – 2 ml/min; H_2 flow – 150 ml/min.

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TABLE I

Reproducibility of Reactions
(Conditions: Temperature – 170 C; Oil Flow – 3 ml/min;
H_2 Flow – 400 ml/min; Cat. – 0.3% Ni)

Run no.	Final FA composition (%) 16:0	18:0	18:1	18:2	18:3	ΔIV	*trans* (%)	k_1	k_2	S.R. k_1/k_2
1	11.0	7.8	56.1	24.6	0.6	41	24.7	1.07	0.48	2.2
2	11.6	6.8	53.9	26.9	0.8	38	21.8	1.16	0.55	2.1
3	11.0	7.0	50.9	29.6	1.6	34	20.5	1.08	0.48	2.3
4	11.5	7.8	55.9	24.5	0.7	41	23.2	1.17	0.58	1.9
5	11.2	7.8	53.9	27.0	0.5	39	24.1	1.13	0.57	2.0
6	11.0	7.5	56.8	24.2	0.5	42	23.5	1.04	0.48	2.2

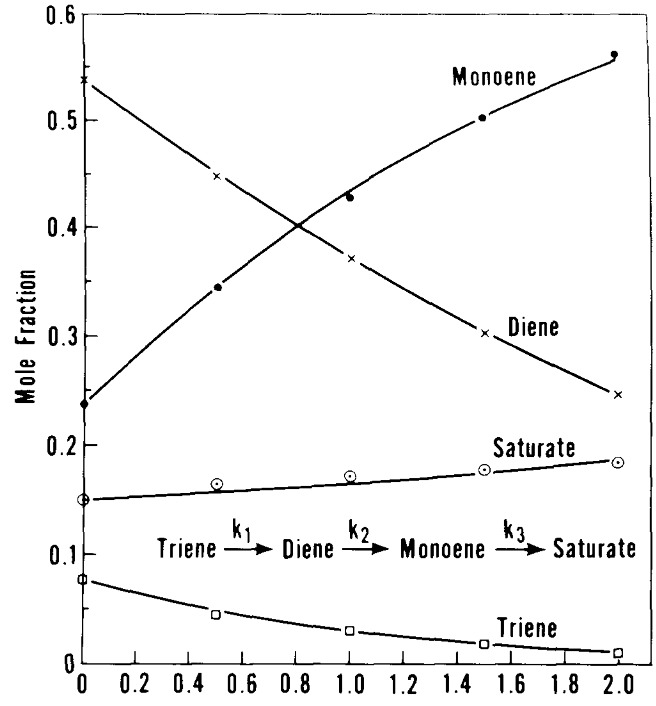

FIG. 2. Continuous hydrogenation of soybean oil. Calculation of reaction rates. Operating conditions are: temperature – 180 C; oil flow – 2 ml/min; H_2 flow – 650 ml/min, 0.3% Ni catalyst.

three variables upon the dependent variables of reaction rate, selectivity, and *trans* content was determined. Equations estimating the dependent variable from the three independent variables were determined and examined for statistical significance. Six additional hydrogenations were also run to check the design, especially the values that were extrapolated outside the region of the experiment.

The partially reduced samples were analyzed as methyl esters with a gas chromatograph equipped with a flame ionization detector using a DEGS column ¼ in. x 5 ft at 190C.. *trans* Content was measured using AOCS tentative method CD 14-61 (9). *cis,cis* Polyunsaturated content of the methyl esters was determined according to Sheppard et al. (10). The methyl esters were separated into *cis* monoene, *trans* monoene, and diene fractions by high performance liquid chromatography methods (11). Total double bond distribution was determined from the sodium borohydride reduced ozonides of the diene and monoene fractions by methods to be published by this laboratory.

RESULTS AND DISCUSSION

The reproducibility of the continuous hydrogenation was demonstrated by six reactions performed at identical conditions. Results of these reactions are presented in Table I.

The following reaction scheme was used to simulate the experimental data from the flow reactor. It was assumed by the model that the reactions were first order and irreversible.

$$\text{Triene}\overset{k_1}{\text{———}}\text{diene}\overset{k_2}{\text{———}}\text{monoene}\overset{k_3}{\text{———}}\text{saturate}$$

Rate constants were calculated so that the sum of the square of the distances between the experimental and calculated composition was a minimum (12). Compositional data for a typical hydrogenation is plotted against the residence time as shown in Figure 2. Experimental data and calculated rate constants for the hydrogenation runs are presented in Table II.

By using the small static mixer, dispersion of the gas was very good; and at the high gas velocities used, no significant interaction between the hydrogen flow rate and the k_1 and k_2 values was apparent. Eldib reported that in batch reactions mass transfer resistances tend to be eliminated at high gas flow rates and with high agitation, and rate of hydrogenation does not increase with additional stirring (13).

Although the extent of hydrogenation was increased by decreasing the oil flow, which resulted in a longer residence time in the reactor, rate constants were not affected by the oil flow rate.

A quantitative relationship between the reaction rates and temperature was shown by the Arrhenius plots in Figure 3. Values for k_1 and k_2 plotted in the figure are the average of those determined for the reaction performed at the particular temperature. The data indicated that reaction rates increase with increase in temperature. The slopes of the curves decrease at higher temperatures in the same way as those reported by Coenen (14). From the average of the slopes the energies of activation were calculated to be ca. 5200 cal/mole for k_1 and 6600 cal/mole for k_2. These values compare with Coenen's 5800 cal/mole for the overall rate of hydrogenation in batch operation. The rate of reduction of linolenate was greater than linoleate; therefore, as expected the activation energy for k_2 was higher (15).

Included in Table II is the selectivity ratio, k_1/k_2, for each run. The various operating conditions of temperature, oil flow rate, and hydrogen flow rate have no significant effect on the selectivity.

The amount of *trans* isomers formed and the extent of hydrogenation were both increased by increasing the temperature or decreasing the oil flow rate. Changes in hydrogen flow rate, however, caused no significant change in either *trans* content or extent of hydrogenation. The dependence of *trans* content upon the extent of reaction was shown by the much smaller change in the specific isomerization, S_i, the number of *trans* double bonds formed per double bonds reduced (16). However, as shown in Figure 3, S_i did increase slightly with temperature between 150 and 170 C.

Samples from the continuous reactor were compared to

TABLE II

Total Hydrogenation[a] Characterization

	Conditions[b]		Results									
			Final FA composition (%)						*trans*			S.R.
Temp. (C)	Oil flow (ml/min)	H_2 flow (ml/min)	16:0	18:0	18:1	18:2	18:3	ΔIV	(%)	k_1	k_2	k_1/k_2
150	2	150	11.1	6.2	45.1	35.3	2.3	28	17.5	0.60	0.32	1.9
150	2	400	11.2	6.1	41.5	38.0	3.2	24	13.7	0.60	0.28	2.2
153	3	400	11.1	6.8	38.5	40.3	3.4	22	12.6	0.62	0.28	2.2
160	2	150	10.9	7.7	52.1	28.1	1.2	37	22.5	0.84	0.38	2.2
160	2	650	11.1	7.5	49.6	30.4	1.4	34	23.0	0.84	0.39	2.2
160	4	150	11.3	6.1	39.0	40.5	3.1	22	13.1	0.80	0.37	2.2
160	4	650	11.2	6.1	38.0	40.9	3.8	21	14.0	0.85	0.36	2.4
170	1.5	400	11.0	7.8	56.1	24.6	0.6	42	28.5	0.97	0.45	2.2
170	2	150	10.7	7.0	53.4	27.8	1.1	37	24.4	1.14	0.52	2.2
170	3	100	11.0	7.0	49.5	31.2	1.4	34	20.9	1.01	0.45	2.2
170	3	400	11.6	6.8	53.9	26.9	0.8	39	23.8	1.16	0.55	2.1
170	3	700	11.0	7.4	52.7	27.1	0.8	39	22.7	1.12	0.56	2.0
170	4.5	400	10.4	5.3	39.0	41.2	4.1	18	11.1	0.97	0.48	2.0
180	2	150	11.1	7.5	61.0	19.9	0.5	46	28.2	1.28	0.56	2.3
180	2	650	11.0	7.3	56.2	24.5	1.0	41	27.7	1.24	0.57	2.2
180	4	150	10.9	6.6	49.4	31.3	1.8	33	19.9	1.29	0.57	2.3
180	4	650	11.9	6.2	45.9	33.6	1.4	32	20.6	1.39	0.58	2.4
187	3	400	11.1	7.4	55.0	25.6	1.0	40	25.1	1.38	0.58	2.4
190	2	150	11.2	6.8	58.0	23.5	0.5	42	27.5	1.50	0.59	2.5
190	3	150	11.2	7.2	55.5	24.5	1.3	40	25.5	1.33	0.61	2.2

[a] Hydrogenation runs were randomized.

[b] 0.3% Ni catalyst was used for all reactions.

TABLE III

Comparison of Reactors

			Reaction	Final FA composition (%)						*trans*
Type of reactor	Temp. (C)	Ni cat. (%)	time (min)	16:0	18:0	18:1	18:2	18:3	ΔIV	(%)
Batch	160	0.3	9	12.2	5.7	48.3	33.3	2.5	30	22.4
Continuous	160	0.3	1	11.3	6.1	39.0	40.5	3.1	22	13.1
Batch	180	0.3	6	10.9	5.8	52.1	28.5	2.7	33	24.7
Continuous	180	0.3	1	10.9	6.6	49.4	31.3	1.8	33	19.9

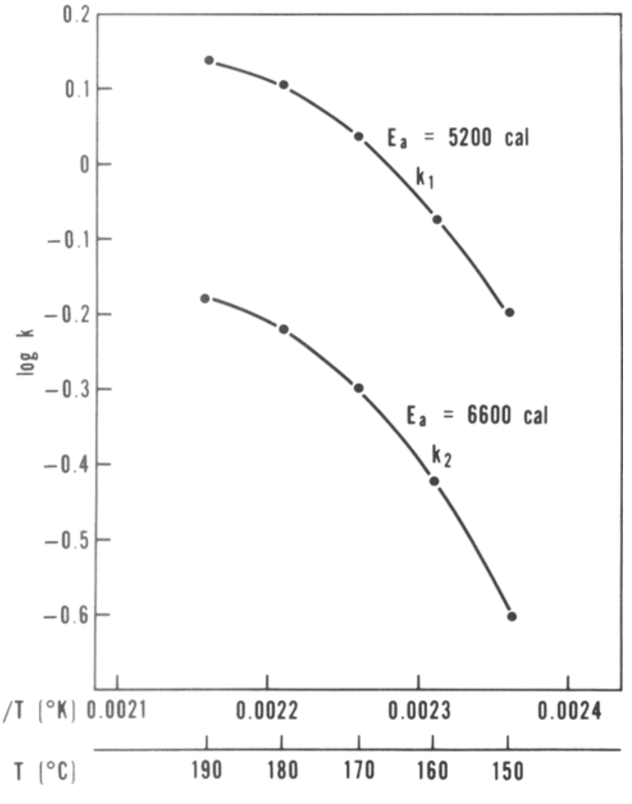

FIG. 3. Arrhenius plots for the continuous hydrogenation of soybean oil.

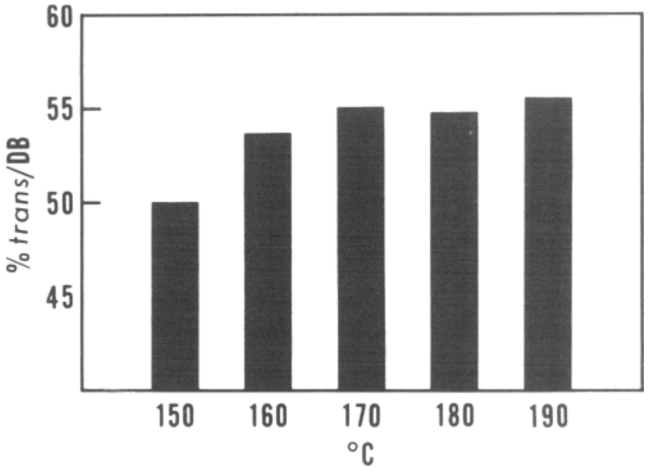

FIG. 4. Specific isomerization (S_i). Amount of *trans* formed per double bond reduced.

those of hydrogenated oils from a batch reactor (17) using the same catalyst concentration and temperature as shown in Table III. If the reactions are considered pseudo-first order in overall rate of reduction, the rate constants calculated for the continuous hydrogenations are 6 to 7 times greater than those for the batch hydrogenations. These pseudo-first order rate constants actually include terms related to mass transfer of oil and hydrogen and hydrogen concentration on the catalyst surface. The ratios of the constants are regarded as indicating excellent mixing of the three phases in the continuous hydrogenation apparatus.

Specific isomerization values, S_i, at 160 C and 180 C were lower for the continuously reduced oil. However, there was no significant difference in the retention of *cis,cis*-polyunsaturates.

Double bond isomerization in countinuous hydrogenation is equivalent to that observed in batch hydrogenations and analyses of commercial hydrogenated oils (18).

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