Laboratory-Scale Continuous Hydrogenation: Effect of Pressure[1]

J.M. SNYDER, T.L. MOUNTS, C.R. SCHOLFIELD and **H.J. DUTTON,**
Northern Regional Research Center, Agricultural Research Service,
U.S. Department of Agriculture, Peoria, IL 61604

ABSTRACT

A laboratory-scale, high pressure, continuous reactor was used to partially hydrogenate soybean oil with copper catalysts. Effects of pressure on the kinetics of the reaction were studied by conducting experiments in a central composite design. The interaction of pressure (75-200 psig) with the other independent variables of temperature (155-255 C) and copper concentration (0.15-1.85%) was evaluated. Dependent variables studied were linolenate selectivity and formation of *trans* isomers and conjugated dienes. In addition, effects of pressure up to 500 psig, use of experimental and commercial copper catalysts and comparison of continuous with high-pressure batch reactions were investigated. Linolenate selectivity (8-10) and *trans* isomer formation were not significantly affected by any of the independent variables. Conjugated dienes were eliminated as products of the reaction when pressure was above 200 psig. Experimental copper-silica catalyst gave a 1.6-fold increase in reaction rate over commercial copper catalysts.

INTRODUCTION

Previous studies of effects of elevated pressure in batch hydrogenation of soybean oil with copper catalysts have shown increased reaction rate, retention of linolenic acid selectivity and elimination of conjugated diene as a reaction product (1,2). Copper-catalyzed hydrogenations using continuous reactors have been reported to have lower linolenic selectivity than comparable reactions in batch converters (3-5). In contrast, our earlier study reported that during continuous hydrogenation at atmospheric pressure, the high linolenic selectivity of copper catalysts was retained; however, conjugated dienes were present in all of the hydrogenated products (6). This paper reports the effects of pressures up to 500 psig on copper-catalyzed, laboratory-scale, continuous hydrogenation of soybean oil.

EXPERIMENTAL PROCEDURES

Apparatus

The pressure system used for these studies is diagrammed in Figure 1. An oil-catalyst slurry (A) was stirred under a blanket of nitrogen and delivered to the reactor by a metering pump (B). A metering valve (C) permitted control of the flow rate of hydrogen gas, which was introduced into the reactor through a 22-gauge needle at a point about 2 in. downstream of the oil entry point. The tubular reactor (D) consisted of a coiled stainless steel tube (40 ft × 1/16 in. id). Low volume, high-pressure "T" valves (E) were positioned 10, 20, 30 and 40 ft from the inlet to permit incremental sampling during hydrogenation. The reactor was mounted in a hot air chamber (F) for temperature control. Insulated thermocouples that were silver-soldered to the reactor tube just ahead of the sample valves provided an indication of the reaction temperature. A 2-L Parr high-pressure vessel (G) served as a receiver and was equipped with a back-pressure valve for pressure regulation. A single lot of refined and bleached soybean oil was used for all hydrogenation experiments.

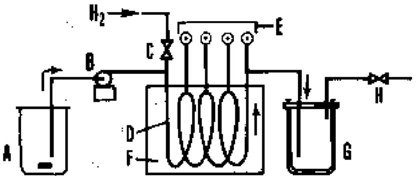

FIG. 1. Schematic of laboratory-scale pressure system for continuous hydrogenation. A: stirred oil-catalyst slurry; B: metering pump; C: hydrogen metering valve; D: tubular reactor; E: sampling valves; F: temperature-controlled air bath; G: receiving vessel; and H: back-pressure valve.

MATERIALS AND METHODS

In a typical experiment, oil containing a suspended copper catalyst was continuously metered at 2.2 mL/min, concurrently with hydrogen gas at 100 mL/min, through the reactor. Prior to induction of the reactants, the hot air bath was controlled to the desired reaction temperature. Flow through the reactor was continued for a minimum of 24 min after thermocouple monitoring indicated temperature equilibration. Since the residence time of the oil in the reactor was estimated to be 12 min, an equilibrium state was assumed and sampling commenced. Careful control of the sampling valve allowed samples to be obtained with minimal variation in reactor pressure. Sampling proceeded first from the valve at the end of the reactor (maximal hydrogenation) and subsequently from the other valves, in turn, until the fourth sample was taken from the valve closest to the reactor inlet. This procedure was designed to minimize the interval of time required to return to steady-state equilibrium prior to taking the next sample. Samples were cooled, filtered from the catalyst and analyzed.

Methyl esters of the partially reduced samples were prepared by transesterification of the oil with sodium methoxide (7). Fatty acid composition was determined using a Varian Aerograph gas chromatograph equipped with a 6 ft × 1/8 in. column packed with 15% EGSS-X on Gas-Chrom P (Applied Science Laboratory). Percentage conjugation was determined by ultraviolet absorption at 232 nm (8). Percentage linolenate was measured by gas chromatography using a 10 ft × 1/8 in. column packed with a 50:50 mixture of 10% OV-17 and 10% OV-225 (9). Infrared spectrometry at 10.3 μ was used to measure *trans*

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content (8). Positional isomerism was determined on the final product from several selected hydrogenation experiments. Methyl esters were separated into *cis*-monoene, *trans*-monoene, and diene fractions by high pressure liquid chromatography (10). Sodium borohydride-reduced ozonides of the monoene and diene fractions were analyzed to determine the extent of isomerization (11). Linolenate selectivity values for each reaction were computed from the compositional data of the oil from each of the 4 sampling valves (12).

Statistical data were based on a central composite experimental design (13). Variable reaction parameters were: pressure: 75, 100, 140, 180 and 200 psig; temperature: 155, 170, 190, 210 and 225 C; and Cu metal concentration in oil: 0.05, 0.15, 0.33, 0.50 and 0.60% (Harshaw Cu-1106P catalyst [39% CuO, 43.5% Cr_2O_3, 10% BaO]). Results obtained from a separate series of continuous hydrogenations using Harshaw Cu-1106P at pressures of 200-500 psig were compared to those previously obtained in batch reactions under the same conditions (2).

The pressure system was applied to an evaluation of the relative activity of 3 catalysts for continuous hydrogenation of soybean oil. A commercial experimental catalyst (38.6% CuO, 32.2% Cr_2O_3, 1.42% MnO) and an NRRC experimental Cu-silica catalyst (33% Cu) (14) were compared to the Harshaw Cu-1106P. Reaction parameters were maintained at 190 C, 140 psig and 0.33% copper.

RESULTS AND DISCUSSION

The reproducibility of the sampling procedure used in these experiments was checked by analysis of duplicate samples from each valve (Table I). When the reaction was at an assumed steady state, the first samples (A) were taken from each valve. The second samples (B) were taken following an equilibration period. The agreement between analyses indicated reproducible sampling. Since there was no preactivation of the catalyst, the initial length of reactor served to activate the catalyst; thus, the analysis of samples from the valve at 10 ft of reactor length showed greater variability than samples from the other 3 valves.

The interaction of pressure with temperature and Cu concentration was evaluated on the basis of the central composite design experiments (13) using nonlinear multiple regression calculations and plotting by a digital computer. Six hydrogenations conducted at identical conditions were performed at random within the experimental design as a measure of the reproducibility of the reactions. Results from these experiments (Table II) indicate excellent reproducibility of the continuous high-pressure reactor. Each value is the mean of the 6 hydrogenations; standard deviation is included in parentheses. Data obtained by analysis of the final product from the continuous hydrogenations are presented in Table III, included is the mean of the 6 replicate reactions in number 10. Standard errors of estimate determined from the regression calculations are given at the bottom of Table III. Data points are significant to the 95% level.

Results of runs 1-4 and 5-8 showed the effects of increasing pressure and temperature at constant catalyst concentration. Total hydrogenation was increased by raising the temperature from 170 to 210 C, but formation of *trans* isomers and linolenate activity remained relatively unaffected. Raising the pressure significantly increased total hydrogenation when the temperature was above 170 C and copper concentration was above 0.16% (runs 12-13 and 14-15); other dependent variables were unaffected. The results of runs 9-11, in which the pressure was increased from 75 to 200 psig while all other parameters were held constant, showed a 5.5-fold increase in ΔIV. Effects of pressure in a tubular reactor can be expected to be different than in a batch reactor, i.e., level of turbulence or agitation may be

TABLE I

Reproducibility of Sampling (100 psig, 190 C, .33% Cu)

		Fatty acid composition				
Valve position (ft)	Sample	Saturate (%)	Monoene (%)	Diene (%)	Triene (%)	Calc. IV.
Original oil		14.5	22.1	55.0	8.4	136.5
10	A	14.5	26.1	51.5	7.9	132.3
	B	14.5	21.9	55.6	7.9	135.9
20	A	14.7	27.3	54.8	3.2	126.6
	B	14.7	27.5	54.2	3.6	126.9
30	A	14.7	29.0	53.8	2.5	124.7
	B	14.9	29.1	53.3	2.7	124.4
40	A	14.9	31.4	52.0	1.7	121.5
	B	14.9	32.1	51.5	1.4	120.6

TABLE II

Reproducibility of Reactions[a] (140 psig; 190 C; 0.33% Cu)

Valve position (ft)	Saturate (%)	Monoene (%)	Diene (%)	Conjugated diene (%)	Triene (%)	ΔIV	*trans* (%)	S_I[b]	S_{II}[c]
10	14.5(0.2)	23.4(0.3)	55.3(0.2)	0.7(0.1)	6.6(0.5)	3(1)	2.2(0.7)	0.82(0.10)	
20	14.4(0.1)	28.0(0.9)	54.3(0.4)	0.8(0.0)	3.3(0.4)	10(1)	7.2(1.0)	0.73(0.07)	
30	14.4(0.0)	31.7(0.2)	52.4(0.1)	0.5(0.1)	1.6(0.1)	14(0)	10.7(0.2)	0.76(0.01)	
40	14.5(0.2)	34.5(0.3)	50.0(0.4)	0	0.9(0.2)	17(1)	13.2(0.3)	0.76(0.02)	9(0)

[a] Each value is mean of 6 hydrogenations; standard deviation is included in parentheses.

[b] Specific isomerization—% *trans*/ΔIV.

[c] Linolenate selectivity (12).

TABLE III

Continuous High Pressure Hydrogenation of Soybean Oil[a]

	Conditions			Fatty acid composition							
Run number	Pressure (psig)	Temp. (C)	Cu (%)	Saturate (%)	Monoene (%)	Diene (%)	Conjugated diene (%)	Triene (%)	ΔIV	S_i	S_{II}
	Original oil	—	—	14.5	22.1	55.0	—	8.4	—	—	—
1	100	170	0.16	14.1	23.2	55.9	0.5	6.8	2	0.80	9
2	180	170	0.16	14.5	23.6	55.8	0.4	6.1	4	0.75	9
3	100	210	0.16	14.5	38.6	46.3	—	0.6	21	0.72	8
4	180	210	0.16	14.3	41.0	44.3	—	0.4	26	0.77	9
5	100	170	0.50	14.5	24.6	55.6	0.8	5.3	5	0.76	10
6	180	170	0.50	14.3	27.4	55.1	0.4	3.2	9	0.75	10
7	100	210	0.50	14.3	49.7	35.9	—	0.1	29	0.76	9
8	180	210	0.50	14.4	55.4	30.1	—	0.1	36	0.76	8
9	75	190	0.33	14.3	31.8	52.7	1.1	1.2	4	0.75	10
10[b]	140	190	0.33	14.5	34.5	50.0	—	0.9	17	0.76	9
11	200	190	0.33	14.8	38.7	46.0	—	0.5	22	0.78	9
12	140	155	0.33	14.3	22.8	55.7	—	7.2	1	—	—
13	140	225	0.33	14.6	59.9	25.5	—	—	40	0.74	8
14	140	190	0.05	14.2	26.2	54.8	0.6	4.8	6	0.77	8
15	140	190	0.61	14.7	41.6	43.3	—	0.4	24	0.75	9
	Standard error[c]								2.3	0.15	.32
	Approximate LSD[d] between runs								7.2	0.47	1.00

[a] Analysis of final product of reaction.

[b] Mean results from 6 hydrogenation runs at identical conditions.

[c] Determined from regression calculations.

[d] Least significant difference (0.05 level).

changed and residence time of the oil in the tube may be affected. The present design of the reactor did not permit a complete evaluation of these factors, and absolute reaction rates were not determined. Studies by Ilsemann and Mukherjee (5) of copper-chromite-catalyzed hydrogenation of soybean oil in a continuous system using oil/catalyst slurries showed low linolenate selectivities (S_{II} = 3-6) and high *trans*-isomer formation (S_i = 1.0-1.6). They reported that raising the temperature increased *trans*-isomer formation, but increased pressure did not affect either linolenate selectivity or formation of *trans* isomers. In contrast, in the present study, the results of all the central composite design experiments (Tables II and III) showed that linolenate selectivity and *trans*-isomer formation were not significantly affected by any of the independent variables.

Formation of conjugated diene was significantly decreased as pressure was increased, as shown by analysis of intermediate samples taken along the length of the reactor (Fig. 2). Included were the data from a copper-catalyzed hydrogenation performed at atmospheric pressure (6). In the latter experiment, conjugated diene content reached a maximum of 5%, but as the pressure was increased, measurable conjugation decreased. In reactions performed above 200 psig, there was no measurable conjugated diene in either the intermediate samples or the final product.

Positional isomerization determined on the monoene and diene fractions isolated from the final products was typical of copper-catalyzed reactions (6). About 90% of the double bonds of the *cis* monoene was located in the Δ9 position, with 2-5% in the Δ10 through Δ12 positions. In the *trans* fractions, the double bonds were concentrated in the Δ10 and Δ11 positions, indicating conjugation mechanism during reaction. No positional isomerization was evident in the diene fraction.

Additional studies were made to compare batch and continuous hydrogenation with pressure varying from 200 psig to 500 psig. Results of analyses of the final product from each hydrogenation are presented in Table IV. Although the batch hydrogenations were conducted to give a constant IV drop (2), the extent of reaction in the continuous system is limited by the fixed length of reactor tube. Nevertheless, there was good agreement for specific isomerization and selectivity values between batch and continuous hydrogenations. Linolenate selectivity remained high and was unaffected by increased pressure. Specific isomerization values (0.80-0.84) are typical of copper hydrogenations performed at pressures above 200 psig (1).

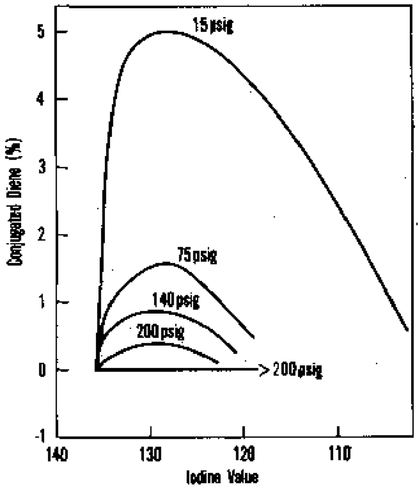

FIG. 2. Effect of pressure on conjugation.

The reaction rate curves plotted in Figure 3 compare the activity of a commercial catalyst (Harshaw Cu-1106P) and the 2 experimental catalysts. Curves of log IV plotted against time of reaction are similar to those obtained previously for copper hydrogenation of soybean oil (1). In these continuous experiments, distance along the length of the tubular reactor was equivalent to time of reaction. The initial reaction of the curve was influenced by the induction period for catalyst activation. Rates of reduction of linolenic and linoleic acid remained constant throughout the

TABLE IV

Comparison of Effects of Pressure in Batch[a] and Continuous[b] Reactors

Type of reactor	Pressure (psig)	Fatty acid composition: Monoene (%)	Diene (%)	Triene (%)	Conjugated diene (%)	Calc. ΔIV	*trans* (%)	S_I	S_{II}
	Original oil	22.2	55.5	8.4	–	–	–	–	–
Batch	200	43.8	42.2	0.1	0.0	26.7	21.0	0.79	10
Continuous	200	24.7	55.3	5.4	0.3	5.0	4.0	0.80	10
Batch	300	43.8	42.2	0.1	0.0	26.7	22.4	0.84	10
Continuous	300	27.3	55.2	3.4	0.0	8.0	6.5	0.81	10
Batch	400	42.6	43.5	0.1	0.0	25.7	21.3	0.83	10
Continuous	400	28.7	54.6	2.5	0.0	10.0	8.4	0.84	10
Batch	500	43.2	42.6	0.3	0.0	26.0	20.6	0.79	9
Continuous	500	29.8	53.8	2.0	0.0	12.0	9.8	0.82	10

[a]Reaction at 170 C, 0.4% Cu (2).

[b]Reaction at 170 C, 0.33% Cu.

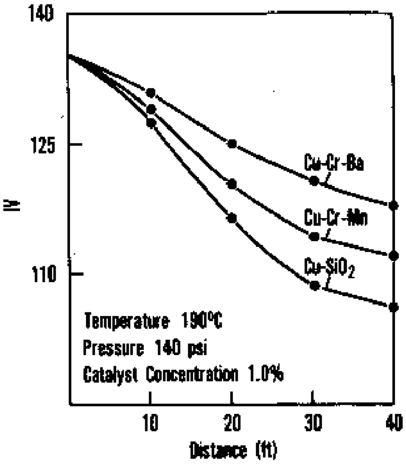

FIG. 3. Relative activity of 3 Cu catalysts.

reaction, with copper catalysts, linolenic acid was reduced 10 times as fast as linoleic acid. The overall rate of change of IV per unit time was a function of the concentration of the individual acid in the oil, thus in the mid-range of these curves, the slope reflected the rate of reduction of linolenic acid. In the final portion of the curve, the slope was influenced by the rate of reduction of linoleic acid. The Harshaw experimental catalyst was 1.3 times and the experimental $CuSiO_2$ catalyst was 1.6 times as active as Harshaw Cu-1106P. Although the data presented were for reactions performed at 140 psig, the relative activity of the catalysts remained the same at the higher pressures investigated.

Commercial application of copper catalyst for the selective hydrogenation of soybean oil has been impeded by low catalyst activity and the formation of conjugated dienes. The results of these experiments demonstrate that continuous hydrogenation at elevated pressures may facilitate the use of copper catalysts. Catalyst activity is increased, linolenate selectivity remains high and formation of conjugated diene is eliminated. Construction of high-pressure batch convertors is considered economically prohibitive, but continuous high-pressure systems should be feasible.

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