Selective Hydrogenation of Soybean Oil: IX. Effect of Pressure in Copper Catalysis[1]

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ABSTRACT

Selective hydrogenation of soybean oil with copper catalyst at 50 psig or less is characterized as a relatively slow reaction requiring higher catalyst concentrations than the less selective but rapid nickel-catalyzed reactions used in most commercial practice. Hydrogenations of soybean oil have been performed which included a high-pressure scan (500, 1000, and 3000 psig), at selected temperatures (110, 130, 150, and 170 C), and at specific catalyst concentrations (0.05, 0.1, 0.2, and 0.4% copper). Selectivities, relative reaction rates, and geometric and positional isomerization have been determined as an evaluation of the effects of high pressure on the kinetics of the reaction. The experimental results indicate that an appropriate selection of pressure, temperature, and catalyst concentration can permit: (a) a significant increase in the rate of reaction while retaining the high linolenic acid selectivity of copper catalysts, (b) use of lower concentrations of copper catalyst while maintaining the higher reaction rate, and (c) elimination of conjugated diene as a measureable product in the hydrogenated oil.

INTRODUCTION

The previous papers in this series (1-8) have reported the capacity of copper catalysts to reduce selectively the linolenate content of soybean oil, studies of the kinetics of copper catalysis, and the preparation of improved types of copper catalysts. Use of copper-chromite catalysts on pilot-plant (9) and plant-scale (10) has been successful in producing edible oils with improved flavor and oxidative stability (11). It has been noted that the copper-chromite and other copper-based catalysts are much less active than the nickel catalysts used in most commercial practice (5,6). This lack of activity and the formation of conjugated diene are serious impediments to the use of copper catalysts in commercial practice.

Eldib and Albright (12) studied the effects of operating variables on the hydrogenation of cottonseed oils using nickel catalyst at pressures up to 140 psig. This research was later extended to relatively high pressures, up to 1500 psig, by Wisniak and Albright (13,14). They reported that raising the pressure of the reaction increased the rate, decreased the *trans*-isomerization, and lowered linoleate selectivity. An earlier publication from our Center reported an investigation of the hydrogenation of soybean oil with copper-chromite catalyst at 75 psig (15). This work suggested that a further study of the effects of pressure on copper catalysis might yield information which would have significance to the application of the catalyst for hydrogenation of edible oils. The present paper is a report of the results of such an investigation.

EXPERIMENTAL PROCEDURES

Materials

Soybean oil: A single lot of refined and bleached soybean oil was obtained from Riceland Foods (Stuttgart, AR)

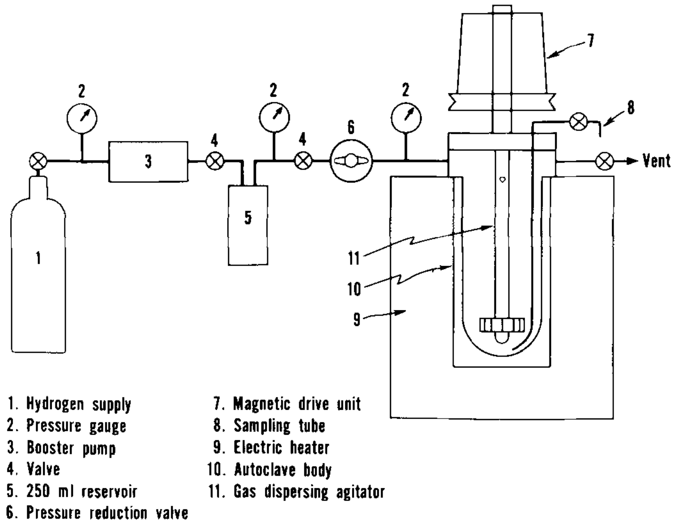

FIG. 1. Hydrogenation apparatus.

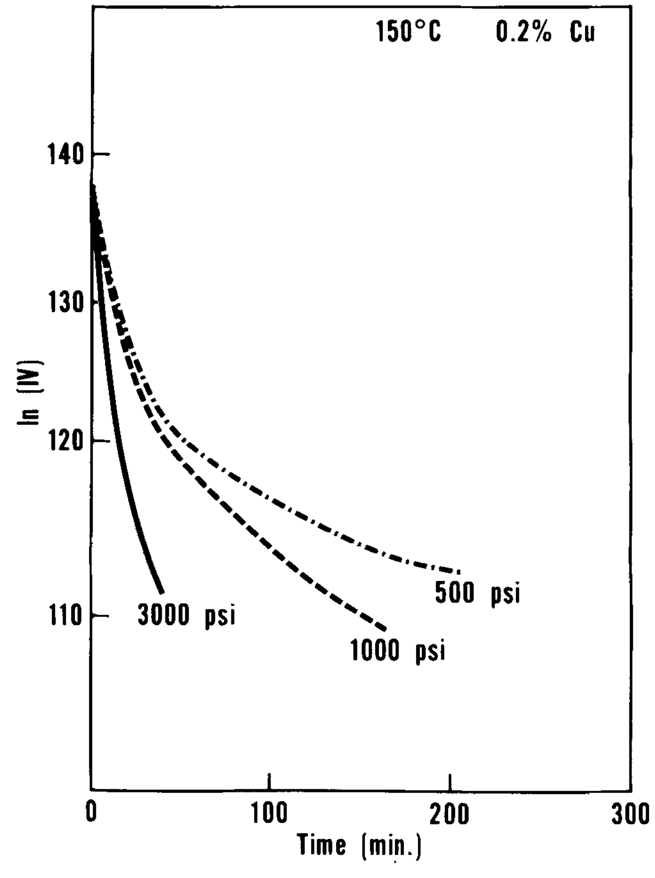

FIG. 2. Effect of pressure on hydrogenation rate.

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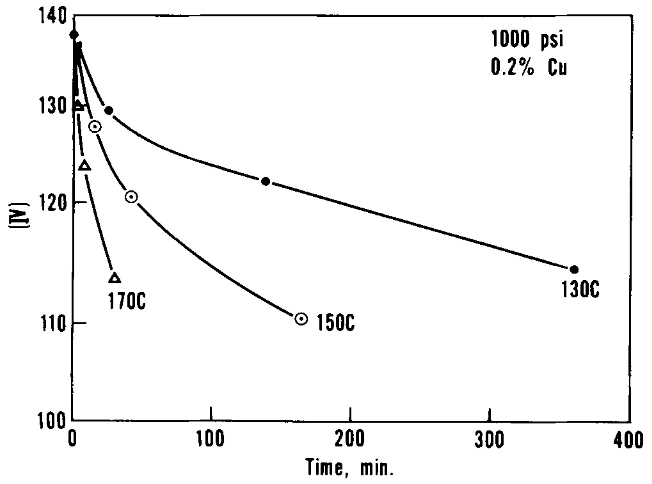

FIG. 3. Effect of temperature on hydrogenation rate.

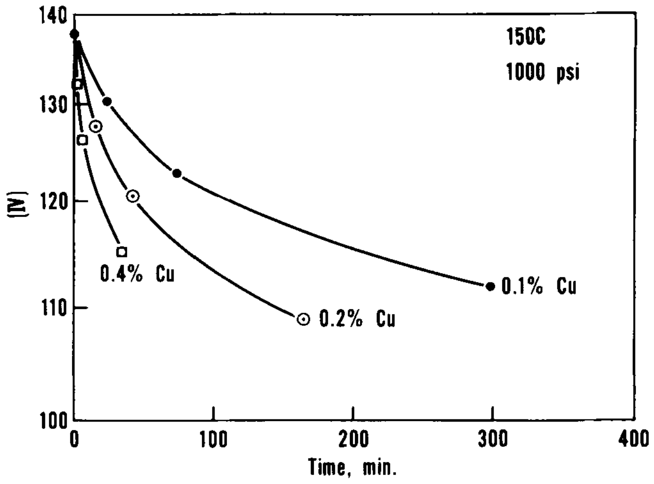

FIG. 4. Effect of catalyst concentration on hydrogenation rate.

and was used in all the experiments reported. The fatty acid composition determined by gas liquid chromatography (GLC) was: 16:0, 10.2%; 18:0, 3.7%; 18:1, 21.5%; 18:2, 56.3%; 18:3, 8.3%. Calculated iodine value was 138.

Catalyst: The hydrogenation catalyst used in these experiments was Cu-1106 P (39% CuO, 43.5% Cr_2O_3, 10% BaO) furnished by the Harshaw Chemical Co., Cleveland, OH.

Methods

Hydrogenation: Hydrogenation reactions were conducted in a 300 ml 316 ss Magne-Drive autoclave manufactured by Autoclave Engineers, Erie, PA. The apparatus is shown schematically in Figure 1. This electrically heated vessel has a safe working pressure of 5000 psig at 650 C and is equipped with a magnetically driven gas-dispersing agitator, internal thermocouple, and sampling tube. Soybean oil (175 g) and copper-chromite catalyst were placed in the autoclave which was then sealed and flushed for 5 min by bubbling nitrogen slowly through the sampling tube while stirring at about 600 rpm. The vessel was then heated to reaction temperature under vacuum with stirring. Hydrogen was introduced through a pressure regulating valve from a 250 ml, 5000 psig, reservoir. Pressure is controlled ±10 psig at 0-1000 psig and ±20 psig at 1000-3000 psig. The agitator speed was increased to 1200-1400 rpm, and three 2-3 ml samples were taken for analysis at predetermined pressure drops (reservoir). The samples are filtered to remove residual catalyst prior to analysis.

Fatty acids: Methyl esters were prepared from triglycerides with sodium methoxide catalyst using a modification of the procedure described by Christopherson and Glass (16) in which ethyl ether replaced petroleum ether. Ester compositions were determined from GLC curves obtained with a Varian Aerograph GC instrument equipped with dual 6 ft x 1/8 in. stainless-steel columns packed with 15% EGSS-X on Gas Chrom P, 100/120 mesh (Applied Science Laboratories, Inc., State College, PA) and with flame ionization detectors. The chromatograph was operated at 185 C with a nitrogen gas flow of 20 ml/min. The analog signal from the detector was fed to a Mod Comp realtime computer programmed to integrate areas under the curves, calculate the composition, and return a formatted report via a laboratory teletype immediately following completion of the chromatogram.

Calculation of rate constants: Relative rate constants were determined by a digital computer assuming consecutive reactions; i.e., triene→diene→monoene (17). Data were fit with respect to average number of double bonds as calculated from compositional data. This method eliminates time as an independent variable and permits only ratios of rate constants to be determined.

TABLE I

Selectivity [K (kLe/kLo)] S_{II}

Temp. (C)	% Cu	500 psig	1000 psig	3000 psig
170	0.1	11	11	—[a]
	0.2	10	10	—
	0.4	9	10	—
150	0.05	—	—	10
	0.1	10	10	10
	0.2	11	9	9
	0.4	10	9	—
130	0.1	—	—	9
	0.2	—	9	9
	0.4	9	8	9
110	0.2	—	—	9
	0.4	—	9	9

[a]— Indicates that experiment was not executed at the reaction conditions because rate of reaction was too fast or too slow.

trans-Isomers: Total isolated *trans* double bond content of the methyl esters was measured by infrared (IR) absorption at 10.36 μ using methyl elaidate as the standard. The methyl esters were separated according to unsaturation by high-performance liquid chromatography (HPLC) (18). Monoene fractions were further separated into *cis* and *trans* fractions on a silver-exchanged resin column (19). Percent *trans* in the monoene was calculated on the basis of weight recovery of *cis*- and *trans*-monoenes. Percent *trans* double bonds in the diene fraction was measured by the same procedure as for total isolated *trans* isomers.

Positional isomers: The double bond distribution in the monoene and diene was determined by reductive ozonolysis followed by GLC analysis of the fragments (Johnston, A.E., H.J. Dutton, C.R. Scholfield, and R.O. Butterfield, unpublished).

Conjugation: The percentage of conjugated double bonds was determined spectrophotometrically by AOCS official method Cd 7-58 (20).

RESULTS AND DISCUSSION

Twenty-four hydrogenations were executed at four temperatures: 110, 130, 150, and 170 C; three pressures: 500, 1000, and 3000 psig; and four catalyst concentrations: 0.05, 0.1, 0.2, and 0.4% copper by weight. Experiments were run in a composite complete block design to assure

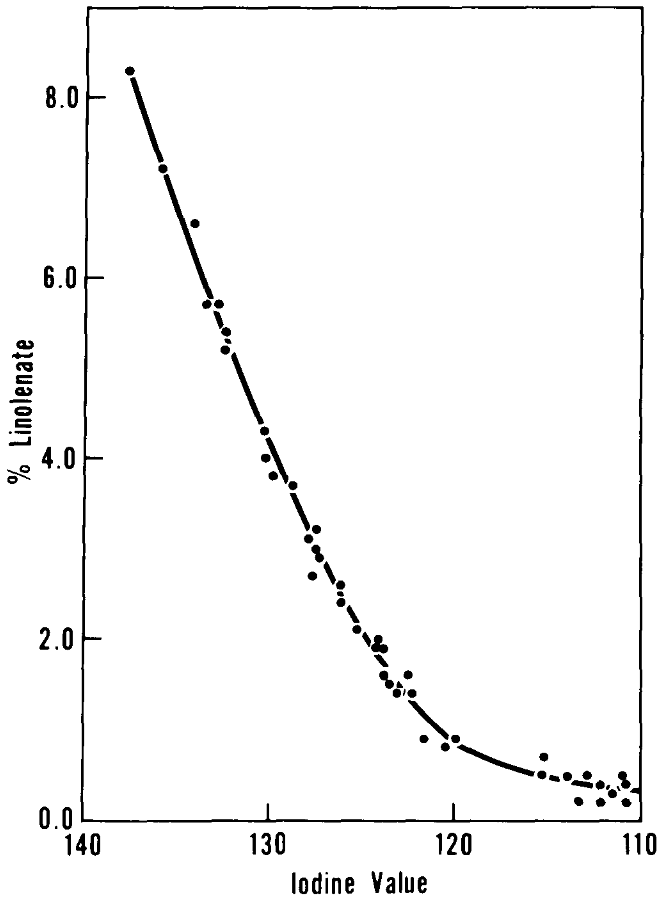

FIG. 5. Linolenic acid vs. iodine value (IV).

statistically significant analysis of all the data. One additional experiment was performed at 205 C, 1000 psig, and 0.05% Cu.

Reaction Rates

As anticipated and as shown in Figures 2-4, a plot of the logarithm of the calculated iodine value (IV) of the oil vs. time indicated that the rate of reaction increased as each parameter was increased. Previous investigators (12,13) had reported that data were represented, with experimental accuracy, by straight lines. They used the negative slopes of the straight lines as being equal to the pseudo first order reaction rate constant. None of the plots of our experimental data is represented by straight lines. The overall reaction rate is the sum of the individual reaction rates. Rates of reduction of linolenic and linoleic acid remain constant throughout the reaction; however, their individual impact on the rate of change of IV per unit time is a function of the concentration of the individual acid in the oil. Copper-catalyzed hydrogenation of soybean oil is, as will be noted below, highly selectivity for reduction of linolenic acid. Thus, during the initial stages of reaction the overall rate of change of IV is a reflection of the rate of reduction of linolenic acid. As the concentration of the linolenic acid is lowered, the rate of reduction of linoleic acid has the greater impact on the observed rate of change of IV.

Selectivity

The linolenic acid selectivity (S_{II}) determined for each experiment is presented in Table I. Final selectivity was over 8 in all experiments. Selectivity ratios are reported to within ±1 unit. Response surface analysis of the data (21) indicated that selectivity decreased slightly as the catalyst concentration was increased. Variations in temperature and pressure, however, had no significant effect. A plot of the percent linolenate vs. the IV for intermediate and final experimental samples, shown in Figure 5, reflects relatively constant selectivity since all points fall on the smooth curve. Previous investigators, studying the hydrogenation of vegetable oil with nickel catalysts, reported that both linoleic acid selectivity (S_I) and *trans*-isomerism decrease when pressure is increased (13).

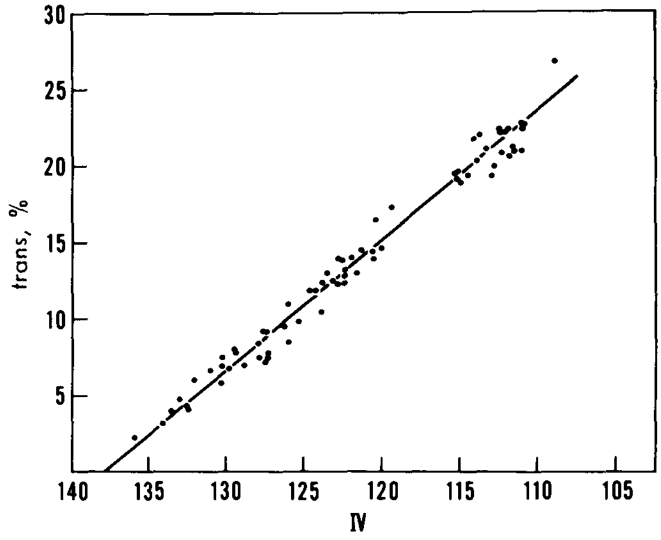

FIG. 6. *trans*-Isomers vs. IV.

trans-Isomerization:

The *trans* analysis (IR) for intermediate and final experimental samples is plotted vs. the IV of each sample (Fig. 6). Total *trans*-unsaturation increases linearly with decrease in IV during hydrogenation. The average specific isomerization value (S_i), defined as the percent *trans* double bonds formed per unit iodine value drop, was calculated to be 0.85 in these experiments. Response surface analysis indicated that this value was not affected by variations of reaction parameters within the ranges studied here. In previous experiments using the same catalyst at 170 C, 30 psig, S_i values of 0.67 (22), 0.56 (2), and 0.57 (23) were observed. The S_i determined for reactions performed at 170 C in these studies was 0.84. This evidence indicates that contrary to previous observations with Nickel catalysts, as mentioned by Wisniak and Albright (13,14), *trans*-isomerization increased during hydrogenation with copper catalyst at these elevated pressures.

Composition

The fatty acid composition of the hydrogenated oils was calculated from the GLC data and the results of the geometric isomer analysis of the monoene and diene fractions isolated by HPLC (18).

The compositions of hydrogenated oils are presented in Table II. As indicated when one operating condition was being studied, the others were held constant. While the amount of total *trans*-isomers formed was dependent only on the extent of hydrogenation, it appears that temperature and pressure had an effect on *trans*-monoene and *trans*-diene formation. The percent *trans*-monoene formed per unit IV drop was 0.42 at 130 C and 0.52 at 205 C. This reflects an apparent increase in *trans*-monoene formation with increase in temperature. The *trans*-diene values per ΔIV were 0.64 at 130 C and 0.41 at 205 C, indicating a decrease in *trans*-diene formation with increase in temperature. As noted in the previous section, the total *trans*-

TABLE II

Fatty Acid Composition of Hydrogenated Oils (0.2% Cu)

Pressure (psig)	Temp. (C)	IV[a] (Calc.)	16:0	18:0	18:1(c)	18:1(t)	18:2(cc)	18:2(5)	18:3	Total trans (IR)
1000	130	114	10.4	4.1	29.6	9.9	30.5	15.0	0.5	21.7
1000	150	109	10.3	3.9	33.0	12.8	24.7	15.1	0.2	26.7
1000	170	112	10.2	3.8	27.8	12.3	33.0	10.7	0.2	22.2
1000	205	112	10.2	3.8	29.0	13.2	33.1	10.4	0.3	22.0
500	150	112	10.3	4.0	25.6	16.3	31.6	11.8	0.4	22.2
1000	150	109	10.3	3.9	33.0	12.8	24.7	15.1	0.2	26.7
3000	150	111	10.3	4.1	34.7	8.5	28.0	13.9	0.5	20.9

[a]Iodine value.

double bonds formed per unit IV drop remained relatively constant over the range of parameters studied here. Thus, a decrease in *trans*-monoene formation is, within experimental error, balanced by an increase in *trans* diene formation. Pressure appeared also to have an effect on the formation of *trans*-monoene and *trans*-diene. At 500 psig, the percent *trans*-monoene formed per unit IV drop was 0.64, while at 3000 psig, it was 0.32; *trans*-monoene formation decreased. Formation of *trans*-diene per ΔIV increased slightly from 0.46 at 500 psig to 0.52 at 1000 psig and 3000 psig. Diene geometric isomers may be *cis,trans; trans, cis;* or *trans,trans.* Hydrogenations of soybean oil performed at 170 C, 30 psi, using the same copper-chromite catalyst produced only minor amounts (2.3%) of diene *trans*-isomers (4). *cis* To *trans* isomerization of the double bonds in linoleate was absent during the reduction of methyl linoleate with copper catalysts at 30 psig (24). In all previous investigations in this series, carried out at lower pressures, conjugated diene was observed as a measurable product (1-3%) of the copper-catalyzed hydrogenation of soybean oil (2). The analysis of these oils hydrogenated at high pressure showed no conjugated diene. This was true for all intermediate samples as well as for the final oil. The reduction of linolenic and linoleic acids through conjugated intermediates is a well-demonstrated mechanism for copper-catalyzed hydrogenations (25). It appears that the rate of reduction of the conjugated intermediates at these elevated pressures is increased so much that they cannot be detected in the oils. Thin layer chromatography of the products of reactions at 205 C, 1000 psig, and 0.2% Cu and at 15,000 psig, 130-170 C, and 0.025-0.1 Cu, showed that no alcohols were formed.

Double Bond Distribution

Figure 7 illustrates the double bond distribution of the *cis* and *trans* monoenes at two of the pressures studied. The amount of monoene having the double bond at position 9 remaining in the oil hydrogenated at 500 psig was 85.1%, while at 3000 psig it was 77.6%. The scattering of the double bonds, as shown here, was less than that reported for *cis* and *trans* monoenes of oils hydrogenated at 30 and 75 psi (15). As would be expected, 10 and 11 isomers predominate in the *trans*-isomer. Previous analyses of the *cis*-monoene fraction of copper-hydrogenated oils has indicated that little, if any, true oleate was formed during the reaction. This finding is supported by the analysis of the *cis*-monoene isolated from the oil reduced at 500 psi. The amount of true oleate calculated from the GLC, *trans* and reductive ozonolysis data (25.6% x 0.851 = 21.5%) was the same as that in the starting oil.

The amount of true oleate calculated for the oil hydrogenated at 3000 psi (34.7% x 0.776 = 26.9%), was greater than that in the starting oil. Thus, for the first time we have evidence indicating, apparently, that true oleate (5-6%) is formed during the reaction.

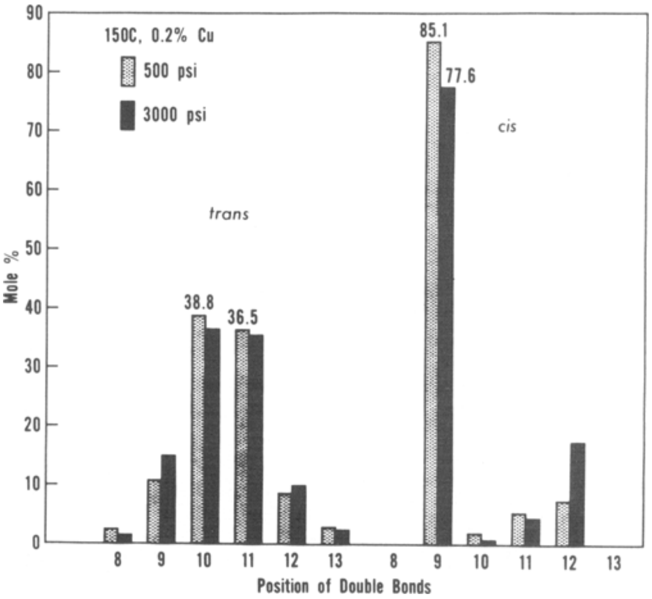

FIG. 7. Double bond distribution in *cis* and *trans* monoenes from selected hydrogenated soybean oils.

The results of these experiments demonstrate that high pressure increases the rate of copper-catalyzed hydrogenation of soybean oil. Unexpectedly, the desirable high selectivity of copper catalysts for reduction of linolenic acid is maintained, and the undesirable reaction product, conjugated diene, is eliminated. While geometric isomerism is increased, positional isomerism is diminished.

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