Technical

Selective Hydrogenation of Soybean Oil: X. Ultra High Pressure and Low Pressure[1]

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ABSTRACT

Soybean oil was partially hydrogenated with copper-chromite catalyst at 170 C and up to 30,000 psig hydrogen pressure. Catalyst activity increased with increase in pressure up to 15,000 psig. The linolenate selectivity (S_{Ln}) of the reaction remained essentially unchanged over 50-1000 psig pressure range. A S_{Ln} of 5.5 to 5.6 was achieved at 15,000 to 30,000 psig pressure range. This value is somewhat lower than the selectivity at 50-1000 psig, but much higher than that obtained with nickel catalysts. Geometric isomerization increased as pressure increased up to 200 psig; above this pressure, the percent *trans* remained the same up to 500 psig. *trans* Isomer content decreased when the pressure was increased to 30,000 psig. *cis,trans* Isomerization of linoleate was greater at 1000 psig and 15,000 psig than at 50 psig. At 15,000 psig, part of the linoleate in soybean oil was hydrogenated directly without prior conjugation, whereas at low pressures, all of the double bonds first conjugate prior to hydrogenation. This difference in mechanism might explain the lower selectivities obtained at high pressures. Conjugated diene isomers were found in the products up to 200 psig. Above this pressure conjugated diene was not measurable. No significant differences were found in the double bond distribution of *trans* monoenes even though the amount of *trans* monoene formed decreased as pressure was increased to 30,000 psig.

INTRODUCTION

Investigations have shown that selective hydrogenation of linolenate in soybean oil could be accomplished with copper catalysts (1–4). However, copper catalysts are not as active at low hydrogen pressures as the commonly employed nickel catalysts. In a previous paper (5), we have shown that increased activity of copper catalysts resulted without loss of selectivity when higher pressures up to 3000 psig were employed. The present paper is, in part, a continuation of these studies which were extended to 30,000 psig.

At low pressures, copper catalysts produce small amounts of undesirable conjugated dienes (6). This drawback can be overcome if higher pressures are employed (4,5). We have, therefore, carried out the reaction at five pressures up to 500 psig in order to determine at what pressure conjugated dienes are eliminated as a measurable product. Kinetic information obtained at these pressures in batch hydrogenation will be useful in the design of continuous reactors which might offer an economic advantage over batch reactors. This report summarizes the results of these studies.

EXPERIMENTAL PROCEDURES

The materials used, the technique of hydrogenation, and the analytical methods employed in this investigation were the same as reported previously (5). At 15,000 and 30,000 psig, the hydrogenation procedure was slightly modified. A

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300 ml Magne-Drive autoclave, which has a safe working pressure of 30,000 psig, was employed. At reaction temperature, agitation was stopped, and hydrogen gas was admitted into the reactor directly from the booster pump. After the desired pressure was reached, the valve was closed and agitation was started. Samples could not be taken at these high pressures. Hydrogenations were carried out at 50, 100, 200, 300, 400, 500, 1000, 15,000, and 30,000 psig hydrogen pressure. The temperature (170 C) of the reaction, weight of the oil (175 g), and rate of agitation (1200–1400 rpm) were kept constant while the catalyst concentration varied from 0.025 go 0.4% copper. When conjugated dienes were produced, the gas liquid chromatography (GLC) composition was renormalized with the linolenate and conjugated diene values obtained by the AOCS Official Method Cd 7-58 (7). Total conjugatable dienes were determined by the AOCS Official Method CD 7-58 except the isomerization reaction was carried out for 1 hr. A Perkin-Elmer 3920 GC instrument equipped with flame ionization detectors was employed to separate the diene isomers by capillary gas chromatography on 150 ft x 0.02 in. I.D. stainless steel columns coated with polyphenyl ether. The column was heated to 190 C and flow controller was adjusted to 9 psi helium pressure. Reaction rates were calculated by a digital computer with the assumption that reactions were consecutive; i.e., triene→diene→monoene (8). Selectivity ratios (S_{Ln}) were calculated from these rate constants.

RESULTS AND DISCUSSION

Low Pressure (50–500 psig) Reactions

Hydrogenations were carried out at different pressures ranging from 50–500 psig. The temperature (170 C) of the reaction, weight of oil (175 g), rate of agitation (1200–1400 rpm), and catalyst concentration (0.4% copper) were kept constant. Three samples were taken at predetermined pressure drops in the reservoir each of which corresponded to an iodine value drop of 7–8 units.

Fatty Acid Composition

The analytical results are shown in Table I. Very little difference was found in fatty acid composition of soybean oil hydrogenated at various pressures. Conjugated dienes were a minor product up to 200 psig. The selectivity of the reaction is virtually the same over the ranges 50–400 psig and slightly diminished at 500 psig. There was no increase in stearate.

Catalyst Activity

The rate of hydrogenation increased with increasing pressure as shown by the reduced reaction times required to drop the IV to 111–112. This increased activity is also

TABLE I

Effect of Pressure on Rat, Selectivity, Conjugation, and Isomerization[a]

| Pressure (psig) | Reaction time (min) | Fatty acid composition | | | | Calcd. IV | % trans | Isomerization index (% trans/ΔIV) | Selectivity (S_{Ln})[c] |
		M[b]	D	T	CD				
50	0	21.5	56.3	8.3	—	137.7	0.0		
	24	27.9	54.4	2.9	1.0	127.5	7.0	0.69	
	87	33.5	51.1	0.9	0.6	120.7	10.7	0.63	10
	360	39.3 (30.0)[d]	46.5 (9.7)	0.3	0.0	115.1	15.5	0.69	
100	8.5	27.1	54.9	3.4	0.7	128.5	6.9	0.75	
	27.5	32.4	52.5	1.1	0.3	122.2	10.5	0.68	10
	180	43.6 (34.3)	42.3 (14.1)	0.2	0.0	111.3	19.2	0.73	
200	7	27.0	55.2	3.4	0.4	128.4	7.0	0.75	
	18	32.1	52.7	1.2	0.0	122.0	11.9	0.76	10
	105	43.8 (34.1)	42.2 (16.9)	0.1	0.0	111.0	21.0	0.79	
300	5	27.3	55.5	3.1	0.0	127.7	7.8	0.78	
	14	32;1	53.0	1.1	0.0	122.3	12.4	0.81	10
	63	43.8	42.2	0.1	0.0	111.0	22.4	0.84	
400	4	26.8	56.0	3.4	0.0	128.9	7.9	0.90	
	11.5	32.2	52.8	1.0	0.0	121.8	12.7	0.80	10
	45	42.6 (31.6)[d]	43.5 (20.4)[d]	0.1	0.0	112.0	21.3	0.83	
500	2.5	27.7	55.0	3.2	0.0	127.5	7.2	0.71	
	6	31.5	53.3	1.4	0.0	123.1	12.5	0.86	9
	38.0	43.2	42.6	0.3	0.0	111.7	20.6	0.79	

[a]Soybean oil (175 g); 170 C and 0.4% copper.

[b]M = monoene; D = diene, T = triene; CD = conjugated diene.

[c]Selectivity (S_{Ln}) = Rate of linolenate hydrogenation/Rate of linoleate hydrogenation.

[d]Values in parenthesis are percent *trans* in monoene and diene fractions.

evident from the plot of log IV vs. time (Fig. 1). Because none of the plots represented straight lines, the reaction is not a true first-order reaction. During the initial stages of hydrogenation, the reduction of linolenate predominated and the rate was high. As linolenate concentration decreased, linoleate hydrogenation became predominant and the rate slowed considerably. Progressive catalyst poisoning could also account for at least part of the change in reaction rate. Unexpectedly, the hydrogenation rates (ΔIV/min) calculated for the final sample (IV 111–112) at each pressure gave a straight line when plotted against pressure (Fig. 2). In this pressure range the rate of reaction is directly proportional to pressure.

Isomerization

Hydrogenation at 50 and 100 psig is accompanied by formation of conjugated dienes. At 200 psig only 0.4% of this isomer was detected in the first sample and none in the later samples. Above 200 psig conjugated diene was not detected during the course of hydrogenation. A plot of conjugated diene vs. iodine value (Fig. 3) shows that the concentration of conjugated diene isomers goes throgh a maximum at each pressure and that the maximum diminishes as the pressure is increased. These results indicate that it should be possible to produce a hydrogenated soybean oil free of conjugated diene isomers if copper catalysts are employed at pressures above 200 psig.

trans-Isomers appear to increase as pressure increases from 50 to 200 psig. The isomerization index (percent *trans*-isomers formed per unit iodine value drop) is a more

meaningful measure of isomerization. At 50 and 100 psig this isomerization index was 0.7. At 200 psig, this value increased to 0.8 and stayed same at higher pressures. The percent *trans* in monoene fractions at 50, 100, and 200 psig was almost unchanged. (Although there was more *trans* monoene formed at 100 than at 50 psig, the percent *trans* monoene was essentially unchanged on the basis of IV
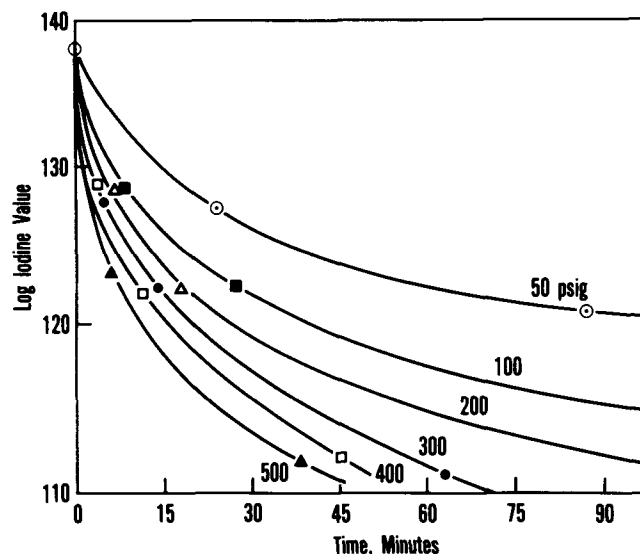

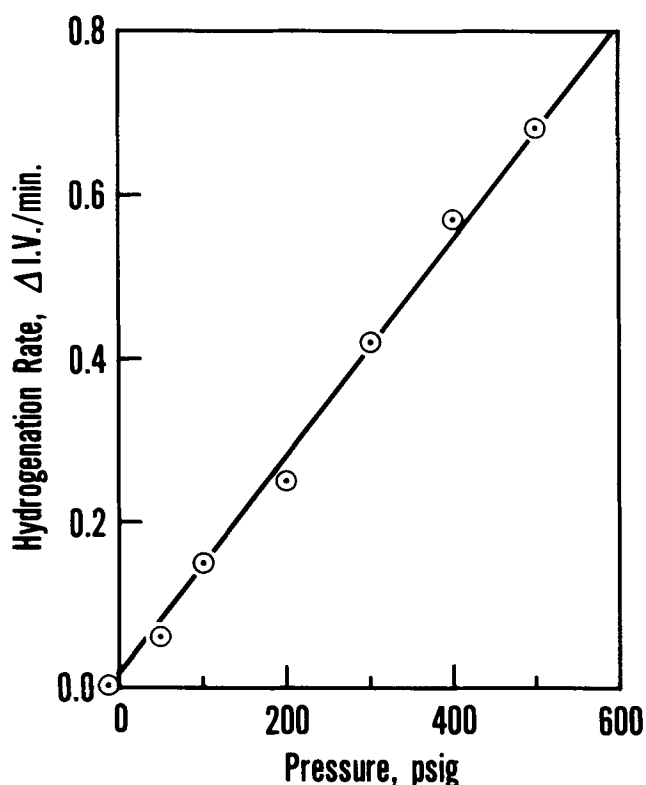FIG. 1. Selective hydrogenation of soybean oil: log IV vs. time.

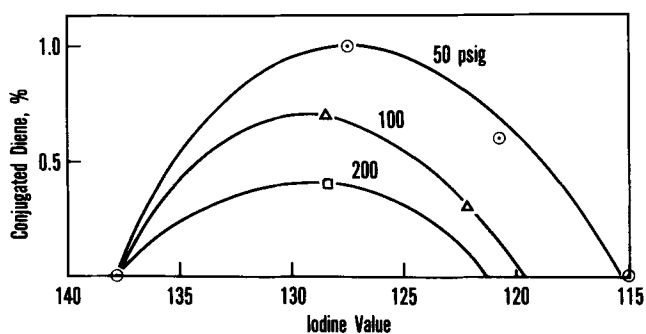FIG. 2. Effect of pressure on hydrogenation rate.

FIG. 3. Change in concentration of conjugated diene with hydrogenation.

drop.) The percent *trans* in the diene fraction, on the other hand, increased from 9.7% at 50 psig to 16.9% at 200 psig (Table I). Therefore, the increase in isomerization index with pressure was due almost entirely to *trans* diene.

The double bond distributions of various *trans*-monoene fractions were found to be typical of the high pressure reactions (5). The Δ^{10} and Δ^{11} isomers derived by hydrogenation of conjugated intermediates were the predominant isomers. This indicates that even though conjugated diene isomers are not found in soybean oil hydrogenated above 200 psig, conjugation prior to hydrogenation is still a predominant pathway as is the case at low pressures (9). One probable explanation for the absence of conjugated dienes above 200 psig is their greater reactivity with hydrogen compared to methylene-interrupted polyunsaturates. The conjugated isomers that are formed on the catalyst surface are hydrogenated before they are desorbed.

The results of this part of the study indicate the possibility of hydrogenation at elevated pressures and at lower catalyst levels without loss in selectivity (S_{Ln}). There will be essentially no change in fatty acid composition. Conjugated dienes will not be a measurable product. Greater catalyst activity can be achieved at the higher pressure and the catalyst can perhaps be reused. One drawback is the increased isomerization of the remaining linoleate in the hydrogenated product. Previous studies on hydrogenation of soybean oil (10) and methyl linoleate (11) at 30 psig showed that such isomerization was negligible.

Present day convertors in the edible oil industry are limited to 100 psig (12) which restricts their use for copper hydrogenation at high pressures. Continuous hydrogenation systems could prove ideal for high pressure hydrogenation. Such a system is probably more economical than a batch system.

Ultra High Pressure Reactions

Analytical results of the hydrogenated oils are shown in Table II.

As the pressure increased from 50 to 15,000 psig, reaction time was reduced considerably even though lower concentrations of catalyst were employed. A more quantitative comparison of catalyst activity can be made from relative catalyst activity, which was calculated as the rate of I.V. drop/min/1% of copper employed and then compared with the value obtained at 50 psig. Thus, it can be seen that catalyst activity increased by 27 times when pressure

TABLE II

Analytical Results of Soybean Oils Hydrogenated at Different Pressures Over Copper-Chromite at 170 C

	Original	50 psig	1000 psig	15,000 psig	30,000 psig
% Copper	—	0.4	0.2	0.025	0.025
Hydrogenation time (min)	---	360	30	50	42
Palmitate	10.2	10.2	10.2	10.3	9.9
Stearate	3.7	3.7	3.8	4.2	4.1
trans Monoene	---	11.8	12.3	5.0	3.3
cis Monoene	21.5	27.5	29.8	37.0	33.8
Diene	56.3	46.5	43.7	42.8	47.4
% *trans* in Diene	—	9.7	24.5	22.6	12.9
Triene	8.3	0.3	0.2	0.8	1.6
Calculated I.V.	137.7	115.1	112.4	112.4	118.1
Relative catalyst activity[a]	---	1	27	129	119
% *trans*	—	15.5	22.2	15.5	8.2
% *trans*/ΔI.V.	---	0.69	0.88	0.61	0.42
Selectivity (S_{Ln})	---	9.9	9.3	5.6	5.5

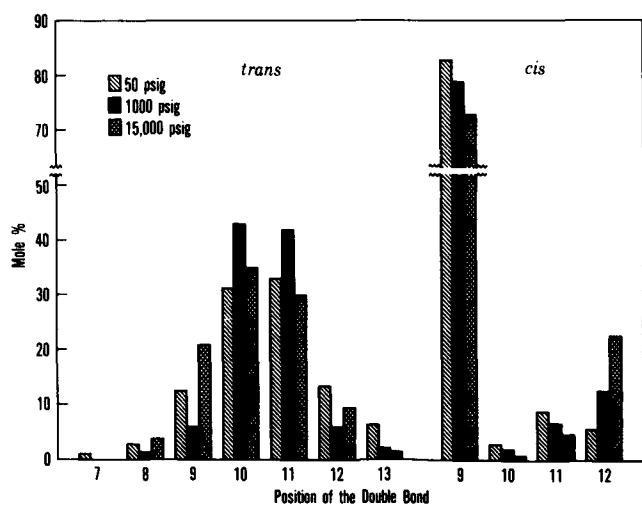[a]I.V. drop/min/1% copper relative to 50 psig.

FIG. 4. Double bond distribution in *cis* and *trans* monoene fractions formed during hydrogenation at various pressures.

increased from 50 to 1000 psig. An even greater increase in catalyst activity was obtained at 15,000 psig. Increasing the pressure above 15,000 psig apparently had no effect on the activity of the catalyst.

The selectivity of the reaction (S_{Ln}) did not change significantly when pressure was increased to 1000 psig (9.3 vs. 9.9); but somewhat lower selectivities of 5.6 and 5.5 were observed at 15,000 and 30,000 psig, respectively. Even these values are considerably higher than that normally achieved with nickel catalysts.

trans Isomer formation is affected by pressure. When pressure was increased from 50 psig to 1000 psig, more *trans* isomers were formed. However, increasing the pressure to 15,000 and 30,000 psig had the opposite effect. A more meaningful measure of *trans* isomer formation is the percent *trans* formed per unit iodine value drop. It can be seen from Table II that this value increased from 0.69 to 0.88 when pressure was increased from 50 to 1000 psig and that this value decreased to 0.61 and 0.42 when the pressure was further increased to 15,000 and 30,000 psig, respectively. Previous work (5) indicated that *trans* isomerization (% *trans*/ΔI.V. = 0.85) did not change in the pressure range of 500 to 3000 psig. Present data clearly show that increasing the presence to 15,000 and 30,000 psig decreased *trans* isomerization considerably.

One undesirable effect of increased pressure and the increased *trans* content is increased isomerization of linoleate. At 50 psig, only 9.7% of the remaining diene had *trans* double bonds. At 1000 and 15,000 psig, 24.5 and 22.6% of the dienes, respectively, were changed to *trans*

TABLE III

Monoenes Formed during Hydrogenation at Various Pressures

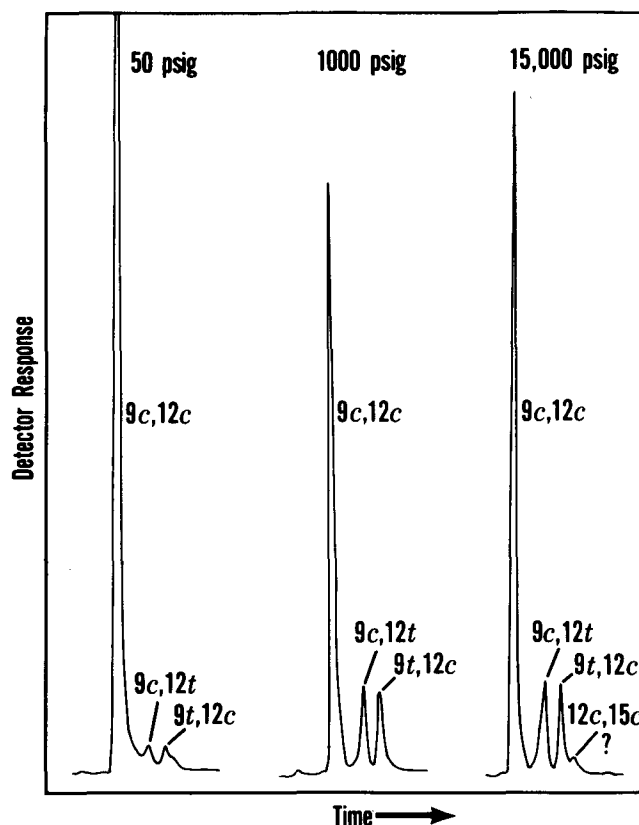| Doubled bond position	50 psig		1000 psig		15,000 psig	
	trans	cis	trans	cis	trans	cis
7	0.1					
8	0.3		0.1		0.2	
9	1.5	22.8	0.8	23.5	1.0	27.0
10	3.6	0.7	5.3	0.6	1.7	0.1
11	3.9	2.4	5.1	1.9	1.5	1.6
12	1.6	1.6	0.7	3.8	0.5	8.3
13	0.8		0.3		0.1	

FIG. 5. Capillary gas chromatograms of diene fractions from soybean hydrogenated at different pressures.

isomers. This trend was reversed above 15,000 psig, and only 12.9% of the diene was isomerized at 30,000 psig. On the other hand, there was no significant change in the amount of *trans* monoene isomers formed when pressure was increased from 50 to 1000 psig. However, at 15,000 and 30,000 psig, considerably less *trans* monoene isomers (5.0 and 3.3%, respectively) are formed compared to 50 and 1000 psig (11.8 and 12.3%, respectively).

The methyl esters of different hydrogenated products were separated into *trans* monoene, *cis* monoene, diene, and saturates as described previously (5). The distribution of double bonds in *trans* and *cis* monoene fractions is given in Figure 4.

The composition of *trans* monoenes formed is not significantly affected by hydrogenation pressure. Δ^{10} and Δ^{11} *trans*-Monoenes are the major products at the three different pressures. These distributions indicate that hydrogenation at all pressures is preceded by conjugation of the double bonds. Δ^9 and Δ^{12} Monoenes are the major products in *cis* monoenes. Δ^9 Monoene in the *cis* fraction is the largest peak because of the large amount of oleate present in the original soybean oil.

Based on the double and bond distribution in Figure 4 and the fatty acid composition of Table II, the amounts of each monoene isomer can be calculated and are shown in Table III.

Considerably more oleate is found in oils hydrogenated at 15,000 psig than is present in the original soybean oil. At 50 and 1000 psig very little, if any, oleate is formed over and above that originally present (22.8% and 23.5%, respectively, vs. 21.5% in original oil). At 15,000 psig, considerably more oleate is found (27% vs. 21.5% in original oil), indicating that at this high pressure some hydrogenation takes place by direct addition of two hydrogen atoms at the 12, 13 double bonds in linoleate. At 15,000 psig,

more Δ^9 + Δ^{12} *cis* monoenes than Δ^{10} + Δ^{11} *trans* monoenes are formed, which again suggests that part of the linoleate in soybean oil is hydrogenated directly without prior conjugation. At low pressures it has been shown that conjugation was an essential first step prior to hydrogenation (9,13). This difference in mechanism might explain the lower selectivities at high pressures (Table II).

Conjugated diene was absent in all fractions as shown by the absence of absorption peak at 233 nm. A major part (96—98%) of the diene had the first double bond at the 9—10 position as indicated by ozonolysis. More than 90% of the dienes (95, 93, and 91% at 15, 100, and 15,000 psig, respectively) were conjugatable as determined by alkali isomerization. These data indicate that for the most part dienes are composed of linoleate and its geometrical isomers. Capillary gas chromatography shown in Figure 5 confirms these results.

The amount of *c,c* 9,12 linoleate estimated from these curves was 92.5, 74.4, and 71.8%, respectively for 50, 1000, and 15,000 psig hydrogenation. Assuming that the remainder (7.5, 25.6, and 28.2%) was composed of geometrical isomers of linoleate, then these values agree reasonably well with those obtained from infrared analysis of dienes (Table II). The discrepancy at 15,000 psig was due to the presence of some *12c,15c* diene isomer (Fig. 5) which was included in the *cis,trans* isomers because the peak was not well separated.

Copper-chromite catalysts are known to catalyze hydrogenolysis of triglycerides. At 170 C and 15,000 or 30,000 psig, we have not detected any alcohols when the hydrogenated products are separated by thin layer chromatography.

The pressures employed in this part of the study are well beyond the practical range. Nevertheless, the results indicate that higher activity with some loss in selectivity can be obtained. Also the lower selectives give *prima facie* evidence that selectivity of copper catalysts is the result of conjugation mechanism.

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