Selective Hydrogenation of Soybean Oil: VII. Poisons and Inhibitors for Copper Catalysts[1]

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ABSTRACT

Hydrogenation rates for the catalytic reduction of soybean oil with a copper-on-silica catalyst increased when the oil was re-refined and bleached in the laboratory. Purification of the re-refined and bleached oil by passage through alumina further enhanced hydrogenation rates. Since these observations suggested that poisons were present in the oil, the effect of minor components of soybean oil upon the activity of copper catalysts was investigated. Free fatty acids, monoglycerides, β-carotene, phosphoric acid, sodium soaps, phosphatides, glycerine, choline, ethanolamine, water, pheophytin, and pyrrole all reduced hydrogenation rates when added to the oil. Organic sulfur added to the oil was a more effective catalyst inhibitor than inorganic sulfur added to the gas. Catalyst activity was affected adversely when iron was added to the oil as a soap or when deposited on the catalyst during its preparation. Squalene, copper soaps, and carbon monoxide had no influence on the activity of the catalyst. Aging of soybean oil also had no effect. There was no significant change in either selectivity or formation of *trans* or conjugated diene isomer when these additives were added to the oil.

INTRODUCTION

Copper-chromite catalysts have been used to hydrogenate undesirable linolenic acid in soybean oil both selectively and successfully on a laboratory (1), pilot-plant (2), and plant-(3) scale. Flavor stability improved considerably by this method (3,4). However, copper-chromite catalysts are much less active than nickel catalysts now employed commercially. Catalysts with improved activity were prepared by supporting copper on high-surface silica (5-7).

A copper-on-silica catalyst gave different hydrogenation rates with different lots of commercially refined and bleached soybean oils. Re-fining and bleaching in the laboratory increased hydrogenation rates (5). Also, when re-refined and bleached oil was purified by passage through activated alumina, still higher hydrogenation rates resulted. These observations suggested that impurities present in the oil adversely affect catalyst activity.

Impurities present in the oil and gas are known to have a deleterious effect on nickel catalyst (8). Some of these impurities include carbon monoxide and hydrogen sulfide in the gas, phosphatides, and sodium soaps in the oil. Because it was not known whether the same impurities poison copper catalysts, the effect of added minor impurities on a copper catalyst was investigated.

EXPERIMENTAL PROCEDURES

Catalyst

The catalyst was copper-on-Cab-O-Sil prepared as described previously (5).

Materials

Refined and bleached soybean oils (free fatty acids [FFA] 0.05-0.06%) came from commercial sources. They were re-refined by adding twice the theoretical amount of 10% sodium hydroxide required to neutralize the FFA. Oil free of FFA was obtained by filtration through Celite. Re-refined oils were bleached with 0.5% Super Filtrol at 105-110 C under 0.5 mm vacuum and filtered through Celite. The resulting oil had an FFA content of 0.01-0.02%. The re-refined and bleached oil was purified by chromatography on alumina. Ca. 400 g oil dissolved in 400 ml pentane-hexane was percolated through a column (2 in. diameter) containing 400 g activated alumina (80-200 mesh). An additional 400 ml pentane-hexane was passed through the column to elute the triglycerides. After solvent was removed from the eluate, the resulting pale yellow oil had an FFA content of 0.00%.

Copper and iron soaps were prepared by double decomposition (9). Commercial soybean phosphatides were recrystallized from chloroform-acetone. Pheophytin was prepared from acidified extracts of spinach (10). β-carotene suspended in vegetable oil was used.

Hydrogenation

Hydrogenations were carried out in a Parr apparatus equipped with a gas dispersion agitator (11) and an external reservoir tank to measure the uptake of hydrogen. The oil (300 ml, 270 g) and the catalyst (0.26 g copper) were charged into the bomb, degassed, and heated under nitrogen to 170 C. The bomb then was evacuated, flushed with hydrogen, and filled to 30 psi. The reaction started when the agitator was started (1700 rpm). After the desired amount of reaction, the oil-catalyst mixture was cooled to room temperature and filtered through Celite. Nonvolatile additives were added to the oil-catalyst mixture before heating commenced. Volatile compounds were introduced into the bomb at the temperature of reaction after flushing with hydrogen and evacuation.

Analytical Methods

Methyl esters were prepared by refluxing the oil with 0.2% sodium methoxide and excess methanol for 1 hr. The percentage isolated *trans* was measured by IR absorption at 10.36 μm of methyl esters in carbon disulfide with methyl elaidate as the standard. Gas liquid chromatography (GLC) was performed with a Varian Aerograph GC instrument equipped with dual 6 ft x 1/8 in. stainless steel columns packed with 15% ethylene glycol succinate methyl silicone polymer (EGSS-X) on Gas Chrom P, 100-120 mesh and with flame ionization detectors. Diene conjugation and percent linolenate were measured by the official AOCS Method (12). Fatty acid compositions were computed from GLC and spectrophotometric analyses. From the composition of the initial and hydrogenated soybean oils, selectivity ratios (K_{Le}/K_{Lo}) were determined with a digital computer, based upon a program written by Butterfield and Dutton (13).

RESULTS AND DISCUSSION

The effect of treating the oil on the rate of hydrogenation is represented in Figure 1. Hydrogen uptake increased

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upon re-refining and bleaching the commercial oil. Further increase in uptake occurred when the re-refined and bleached oil was purified by chromatography on alumina. Results were similar with other lots of commercially refined and bleached soybean oils.

Results of hydrogenation of three commercially refined and bleached soybean oils and the effect of re-refining and bleaching them or of purifying them by passage through alumina are given in Table I.

Catalyst activity varied for all three oils, but, when these were re-refined and bleached in the laboratory, all showed a greater activity. Highest activity of the catalyst was exhibited by the oils when they were purified by chromatography on alumina. These treatments had no significant effect on selectivity of reaction; nor was there any change in *trans* or conjugated diene isomer formation, except with alumina-purified oils which produced higher amounts of conjugation.

To test the effect of impurities upon hydrogenation, it would be ideal to start with pure triglycerides like those obtained by chromatography on alumina. However, because of the tedious work involved in preparation of these samples, laboratory re-refined and bleached oils served as starting materials. The influence of added impurities on catalyst activity, selectivity, and isomer formation was evaluated, and the results appear in Table II.

Catalyst activity was calculated in iodine value drop/min relative to the control (without impurity) which was taken as unity. Re-refining and bleaching reduced both color of, and FFA in, the oil. When either FFA or β-carotene or both were added back to the oil, catalyst activity diminished. Addition of 500 ppm β-carotene or 1000 ppm FFA more than doubled the reaction time. Addition of increased amounts of β-carotene or FFA increased the poisoning effect. Inclusion of both β-carotene and FFA decreased catalyst activity more than when either alone was added. Squalene, which is known to be present in soybean oil (14-16), had no effect upon the catalyst. Up to 200 ppm of copper soap dissolved in the oil was not deleterious to the catalyst. Organic sulfur, if present in the oil, is more detrimental than inorganic sulfur present in the gas. Ca. 50 ppm sulfur added to the oil as dodecantethiol diminished catalyst activity considerably and even reduced selectivity of hydrogenation. When the same amount of sulfur was added as hydrogen sulfide, the poisoning effect was not so great as organic sulfur.

Phosphorus compounds when added as phosphatide, phosphoric acid, or phosphatidyl insitol retarded hydrogenation. More than half the catalyst activity was lost upon addition of 15 ppm phosphorus as phosphatide to the oil. Choline and ethanolamine, which may be present in soybean oil as degradation products of phospholipids, acted as catalytic poisons. Both monostearin and glycerol, which are hydrolytic products of triglycerides, also had an inhibitory effect upon hydrogenation.

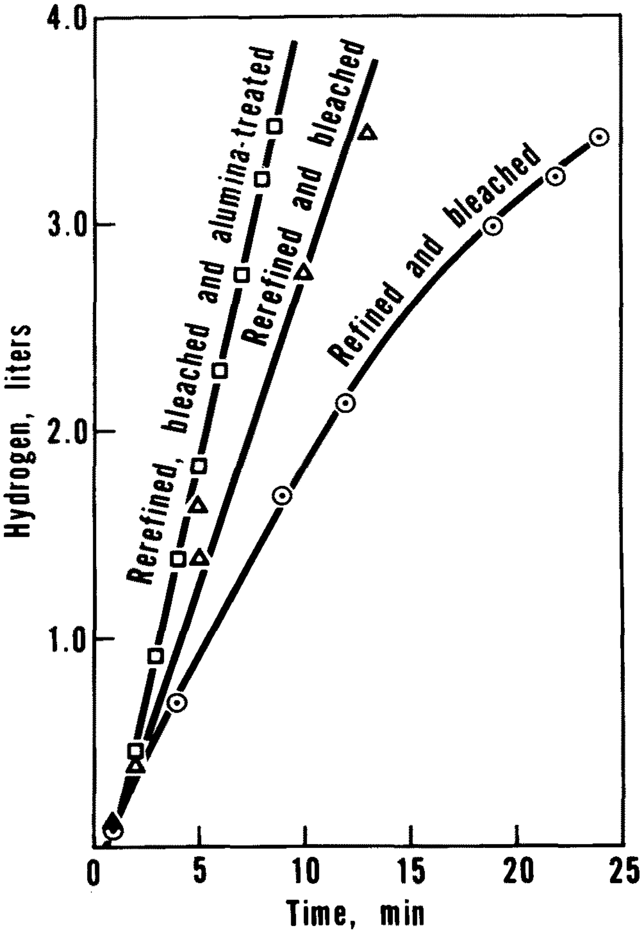

FIG. 1. Effect upon hydrogenation rates of further treatment of a commercially refined and bleached soybean oil.

Sodium ions and water decreased the rate of hydrogena-

TABLE I

Effect of Treatment of Soybean Oils upon Hydrogenation[a]

Soybean oil	Reaction time, min	IV[b] drop	Linolenate %	Diene conjugation %	*trans*, %	Selectivity, K_{Le}/K_{Lo}
Commercial A	42	15	0.6	0.8	11	13
Commercial B	43	15	0.3	1.0	10	14
Commercial C	24	15	1.1	1.2	10	12
A–re-refined and bleached	13	15	0.6	1.5	9	13
B–re-refined and bleached	14	14	0.4	1.4	8	15
C–re-refined and bleached	13	16	1.0	1.5	9	12
A–re-refined, bleached and alumina treated	9	16	0.5	2.4	8	14
B–re-refined, bleached and alumina treated	9	15	0.3	2.3	8	15
C–re-refined, bleached and alumina treated	9	15	0.7	3.0	7	14

[a] 300 ml (270 g) oil at 170 C, 30 psig and 1700 rpm; catalyst–10% copper-on-silica (0.26 g copper).

[b] IV = iodine value.

TABLE II

Effect of Added Impurities upon Hydrogenation[a]

Re-fined and bleached oil plus	Reaction time, min	IV[b] drop	Linolenate, %	Diene conjugation %	*trans*, %	Selectivity, K_{Le}/Lo	Relative catalyst activity
None	13	15	0.6	1.5	9	13	1.00
100 ppm β-carotene[c]	19	15	0.5	1.3	9	13	0.68
500 ppm β-carotene	27	16	0.5	1.2	10	13	0.51
500 ppm Free fatty acids	17	15	0.5	1.4	9	13	0.76
1000 ppm Free fatty acids	30	15	0.6	1.0	8	14	0.44
1000 ppm Free fatty acids + 500 ppm β-carotene	37	15	0.5	1.2	8	14	0.35
1000 ppm Squalene	12	15	0.5	1.2	8	14	1.08
None	14	14	0.4	1.4	8	15	1.00
100 ppm Copper soaps	14	14	0.4	1.5	8	15	1.00
200 ppm Copper soaps	13	13	0.5	1.4	8	15	1.00
10 ppm Sulfur as octadeanethiol	21	13	0.7	1.9	8	13	0.62
20 ppm Sulfur as octadecanethiol	27	12	1.0	1.6	8	11	0.44
50 ppm Sulfur as dodecanethiol	75	9	3.0	2.0	4	9	0.12
25 ppm Sulfur as hydrogen sulfide	17	13	0.6	1.2	9	13	0.76
50 ppm Sulfur as hydrogen sulfide	22	13	0.6	1.5	8	13	0.59
200 ppm Phosphatide (6 ppm phosphorus)	16	13	0.7	1.4	8	13	0.81
500 ppm Phosphatide (15 ppm phosphorus)	26	12	0.8	1.2	8	12	0.46
100 ppm Sodium soap (7 ppm sodium)	18	13	0.7	1.4	8	13	0.72
200 ppm Sodium soap (14 ppm sodium)	28	12	0.9	1.2	7	13	0.43
46 ppm Carbon monoxide	15	13	0.6	1.5	8	14	0.87
Aged soybean oil PV[d] 10.3	14	13	0.7	1.6	8	12	0.93
10 ppm Pheophytin	18	14	0.5	1.1	9	13	0.78
20 ppm Pheophytin	23	13	0.7	1.1	9	12	0.56
10 ppm Pyrrole (2 ppm nitrogen)	40	14	0.9	0.7	9	11	0.35
None	13	16	1.0	1.5	9	12	1.00
100 ppm Iron deposition on catalyst	50	14	1.9	0.7	9	9	0.23
25 ppm Iron deposited on catalyst	22	15	1.5	1.1	9	10	0.55
10 ppm Iron deposited on catalyst	12	16	0.8	1.6	9	13	1.08
25 ppm Iron as soap	23	15	1.0	1.2	8	12	0.53
10 ppm Iron as soap	20	16	0.9	1.3	9	12	0.65
400 ppm Water	18	16	1.1	1.6	8	11	0.72
10 ppm Nitrogen as choline	29	15	1.1	0.8	9	12	0.42
5 ppm Nitrogen as choline	20	15	1.0	1.0	8	12	0.61
5 ppm Nitrogen as ethanolamine	22	16	0.8	1.1	9	13	0.59
500 ppm Monostearin	24	18	0.5	1.0	9	13	0.61
500 ppm Glycerin	25	13	0.9	1.7	8	13	0.42
100 ppm Phosphoric acid (32 ppm phosphrous)	21	15	1.1	1.5	8	12	0.58
270 ppm Phosphotidyl insitol (10 ppm phosphrous)	35	15	1.1	1.1	8	12	0.35
26 ppm Oxygen	32	16	1.0	1.6	8	12	0.41

[a] 300 ml (270 g) oil at 170 C, 30 psig and 1700 rpm; catalyst-10% copper-on-silica (0.26 g copper).

[b] IV = iodine value.

[c] All additives are expressed as ppm on the basis of oil.

[d] PV = peroxide value.

tion. Alkali refining introduces these two substances as contaminants in oils; while water is easily removed under vacuum, it requires a proper bleaching operation to reduce the soap content to acceptable levels. When the oil was aged at 60 C for 1 week (peroxide value = 10), no noticeable poisoning effect was observed. Although the introduction of 46 ppm carbon monoxide had no effect upon hydrogenation, addition of 26 ppm oxygen more than doubled the reaction time. Pheophytin and pyrrole, degradation products of chlorophyll, increased the time of hydrogenation. The oils containing pheophytin turned green after hydrogenation, presumably owing to the formation of copper chlorophyll. Some, but not all, the color was removed by post-bleaching.

Iron was added either to the oil as soap or to the catalyst during its preparation. In both instances, diminished catalyst activity resulted. Deposition of 10 ppm iron on the catalyst did not change its activity. However, addition of 10 ppm iron to the oil markedly decreased catalyst activity.

There was no significant change in the amount of *trans* or conjugated diene isomer formation when impurities were added to the oil. Selectivity also was not altered, except when extensive amounts of impurities were added. It appears that these substances inactivate the catalyst by adsorption on the active sites.

The impurities that have a deleterious effect upon the catalyst are unlikely to be present in the oils at the levels used in Table II. But the presence of even a fraction of all the added impurities will have a cumulative effect upon the catalyst. Most of these impurities could be removed effectively by adequate refining and bleaching.

The carotenoid pigments and FFA that poison coppper have no ill effect upon nickel catalyst (8). Phosphoric acid up to 1000 ppm actually increased hydrogenation rates with a nickel catalyst (17). Large amounts of *trans* isomers are produced when nickel was poisoned with sulfur, whereas sulfur poisoning of copper did not increase *trans* isomer formation. Nickel is susceptible to carbon monoxide which had no effect upon the copper catalyst.

In large scale hydrogenations with copper catalysts, it would be advantageous to start with relatively pure oil so as to require less catalyst. Although chromatography on alumina is the best means of removing catalytic poisons, it may be prohibitively costly. However, more thorough refining and bleaching than is normally practiced for nickel hydrogenation may increase hydrogenation rates sufficiently to offset the added cost of purifying the oil.

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