Selective Hydrogenation of Soybean Oil in the Presence of Copper Catalysts

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Abstract

Many investigators associate the poor keeping properties of soybean oil with its linolenic acid content. On the other hand the high linoleic acid content is a desired property from a nutritional point of view. We have therefore developed a process for the preferential reduction of the linolenic acid content by selective hydrogenation. Conventional catalysts for the hydrogenation of fats have a rather low selectivity in this respect. When linolenic acid in soybean oil is hardened (e.g., with a nickel catalyst), most of the linoleic acid is converted into less unsaturated acids.

It was found that linolenic acid is hydrogenated much more preferentially in the presence of copper catalysts than in that of nickel and other hydrogenation catalysts. At a linolenic acid content of 2%, soybean oil hardened with nickel catalyst contained about 28% linoleic acid, whereas with copper catalyst the hardened soybean oil contained 49% linoleic acid.

By means of our process it is possible to manufacture a good keepable oil of, e.g., I.V. 115 and containing 1% linolenic acid and 46% linoleic acid. The storage stability of this product is comparable with that of sunflower-seed oil. A liquid phase yield of 86% is obtained after winterization at 5C for 18 hr.

The high selectivity for linolenate reduction of copper catalysts must be ascribed to the copper part of the catalyst. Investigations into the structure of the catalyst indicate that the active center consists of copper metal crystallites; whether these centers are promoted by the carrier or traces of other substances is under investigation.

Introduction

SINCE THE SECOND WORLD WAR much biochemical and biological research work has been done on the influence of the fatty acid composition of fats on cardiovascular abnormalities. The results of this work have convinced many investigators that higher levels of polyunsaturated fatty acids in fats are able to inhibit the development of these abnormalities. Consequently, in the past few years margarines with a high polyunsaturated fatty acid content have been marketed. One of the most attractive oils for the production of such margarines is soybean oil, since it contains about 8% linolenic acid and 50% linoleic acid. However, taste and keeping quality of soybean oil are unsatisfactory so that it cannot be incorporated in margarine compositions in large quantities. Since there is evidence that oxidation products of linolenic acid are responsible for the poor flavor stability of soybean oil (4), it is generally believed that by preferential elimination of linolenic acid an oil of good taste, keeping quality and high nutritive value can be obtained (3). Linolenic acid can be eliminated completely by hardening soybean oil in the presence of a nickel catalyst. However, most of the linoleic acid is then also converted into less unsaturated acids so that the biological value of the oil is lowered. Therefore, many investigations have been devoted to a more selective hydrogenation of linolenic acid in soybean oil in such a way that most of the natural linoleic acid (9 *cis*, 12 *cis*-octadecadienoic acid) would be saved.

The selectivity of a catalyst for the hydrogenation of the linolenic compounds (S_L) is usually defined as the ratio of the rate constants of the linolenic and linoleic acid hydrogenation (2): $S_L = k_{Le}/k_L$ (for calculation, see next section).

In the United States, where an important part of the world stock of soybean oil is produced, great interest is shown in the selective hydrogenation of linolenic acid in soybean oil (6,7,13–20,23). Johnston et al. (6) investigated commercially available catalyst (nickel, palladium and platinum on different carriers) in hydrogenating a linoleate-linolenate equimixture and found S_L-values between 1.33 for platinum on carbon at 25C and 2.71 for nickel catalyst at 140C. Willard and Martinez (23) tried to establish the conditions under which the natural linolenic acid (9 *cis*, 12 *cis*, 15 *cis*-octadecatrienoic acid) is hydrogenated into the natural linoleic acid virtually without formation of other unsaturated fatty acids. They investigated different types of catalysts, including reduced nickel oxide, reduced nickel oxide poisoned with cupric acetate, copper chromite and palladium-lead catalysts. In all hydrogenations only minor amounts of natural linoleic acid were formed. Riesz and Weber (13) tried to hydrogenate linolenic acid in soybean oil preferentially. The reaction conditions were varied within wide limits. The investigation comprised nickel, platinum, palladium and rhodium catalysts. The maximum value of S_L found was 2.9 for a palladium-on-carbon catalyst.

About 5 years ago it was discovered in our laboratory that copper catalysts are extremely selective in reducing the linolenic acid content of soybean oil (22). With these catalysts S_L-values varying from about 7 to 14 were found. A small part of this work has already been published (8). In the present paper we will discuss our work on the selective hydrogenation of soybean oil with copper catalysts more extensively.

In the meantime a short communication of Koritala and Dutton (9) appeared—followed by a more detailed publication (10)—drawing attention to the selectivity aspects of a copper chromia catalyst activated with sodium borohydride. Their results are in line with our experience obtained with other copper chromia catalysts.

Tsutomu Kuwata et al. (12) examined the properties of copper chromium manganese oxide catalysts in hydrogenating soybean oil. In their patent they claim a process for improving flavor and taste of soybean oil by reducing the linolenic acid content to zero at an I.V. of 110–115 by means of said catalyst.

Determination of Selectivity Characteristics

The hydrogenation of linolenic acid (Le) and linoleic acid (L) in soybean oil to oleic acid and its isomers (O) may be represented by the following scheme (consecutive first order reactions):

$$\text{Le (triene)} \xrightarrow[k_{Le}]{+H_2} \text{L (diene)} \xrightarrow[k_L]{+H_2} \text{O (monoene)}$$

In this scheme it is assumed that any isomer of Le and L formed during the hydrogenation are as reactive as the Le and L originally present.

For the above reaction scheme the following equations are valid:

$$\frac{dLe}{dt} = -k_{Le}\ (Le)$$

and

$$\frac{dL}{dt} = -k_L\ (L) + k_{Le}\ (Le)$$

After integration we obtain:

$$(Le) = (Le)_o\ e^{-k_{Le}t} \qquad [1]$$

and

$$(L) = (Le)_o\ \frac{S_L}{1 - S_L}\left\{e^{-k_{Le}t} - e^{-k_L t}\right\} + (L)_o\ e^{-k_L t} \qquad [2]$$

in which (Le) and (L) are the concentrations of Le and L at time t, $(Le)_o$ and $(L)_o$ the concentrations of Le and L at time $t = 0$, and S_L is the ratio of the first order reaction constants k_{Le} and k_L.

For an oil whose composition before and after hydrogenation is known (determined by GLC-analysis), the value of S_L can be calculated from equations 1 and 2.

The above kinetics do not pretend to reflect the mechanism of this very complex hydrogenation. It has only been introduced to define a compact selectivity parameter, which is almost independent of the degree of hydrogenation.

During hydrogenation isolinoleic acids (geometric and positional isomers) are also formed which cannot be readily separated by gas chromatography; therefore, the amount of natural linoleic acid cannot be derived from GLC-data alone. A rough approximation can be obtained by determining the amount of alkali-conjugatable linoleic acid. Since besides the *cis,cis*-double bonds separated by a methylene group, *cis,trans* and to a lower degree *trans, trans*-double bonds are also conjugated, this method will give too high values for the desired natural linoleic acid content.

For a more exact determination the isotope dilution method was used (1): a known amount of ^{14}C-labeled 9 *cis*,12 *cis*-octadecadienoic acid is added to the fatty acid mixture to be examined, the mixture is brominated, and the tetrabromide derivative of 9 *cis*,12 *cis*-octadecadienoic acid is then isolated and purified by crystallization. From the ratio of the specific radioactivities of the tetrabromide compound and the model compound, the natural linoleic acid content can be calculated. This method is independent of the yield of the tetrabromide derivative.

Hydrogenation of Soybean Oil With Copper Catalysts

Starting Materials

Most of the catalysts used in the experiments to be described here were made by coprecipitation of copper sulfate and magnesium sulfate from aqueous solution by the addition of an aqueous solution of sodium silicate and sodium carbonate. The catalyst thus obtained was filtered off, washed and dried.

Since activated copper catalysts are easily poisoned (e.g., by water and free fatty acids), the starting oil to be hardened must be thoroughly prerefined. The treatment applied consisted of degumming, neutralization and bleaching with active earth; during the last step the product is also dried. This prerefining procedure does not differ much from that applied in conventional nickel hardening.

Hardening Procedure

The hardening procedure with copper catalysts does not differ essentially from conventional nickel hardening. The same equipment may be applied, provided that this equipment can be used at a pressure of 3 to 10 atmospheres. Although the selectivity in copper hardening does not depend much on the hydrogen pressure, less conjugated diene isomers are found at a somewhat higher pressure.

The main technical difference between nickel and copper hardening is that the copper catalyst can be activated in the initial stage of the hardening process at a temperature of about 180C (wet activation), whereas the nickel catalyst has to be activated outside the hardening vessel (in the case of supported nickel catalysts the activation occurs by reducing the catalyst with hydrogen at a temperature of about 400C; in the case of nickel formate catalyst the activation occurs by decomposition in fat at a temperature of about 240C).

In Table I a typical example is given of a hardening of soybean oil with copper catalyst. For this experiment a value for $S_L = 14$ was calculated from the fatty acid composition.

Postrefining of Copper-Hardened Products

It has been long known that traces of copper present in oils and fats catalyze oxidation reactions so that the taste and storage stability of the oils are greatly impaired. These traces must therefore be removed as thoroughly as possible. Apart from this aspect the postrefining of copper-hardened products does not present special problems compared with those encountered for nickel-hardened products.

After hardening, the catalyst is filtered off and the copper content in the oil is reduced to less than 0.1 mg/kg by washing with, e.g., phosphoric acid. Finally the oil is washed with water and subjected to conventional deacidification, bleaching and deodorization.

Results and Discussion

Selectivity of the Copper Hardening

In Table II examples of copper hardening of soybean oil to different iodine values are given.

Table II shows that the S_L-values of ca. 10 reached in copper hardenings are far higher than those

TABLE I

Hydrogenation of Prerefined Soybean Oil with Copper Catalyst (0.1% Cu on oil) at 185C and 5 Atmospheres Gauge Pressure H_2 During 30 Min

Composition	Starting oil (I.V. 134) wt %	Hardened oil (I.V. 112) wt %
Linolenic acid (C_{18} triene)	8.5	Trace
Linoleic acid (C_{18} diene)	52.5	45.0
Oleic acid (C_{18} monoene)	24.0	39.0
Stearic acid (C_{18} sat.)	4.0	4.0
Palmitic acid (C_{16} sat.)	11.0	11.0

TABLE II

Fatty Acid Composition and Amount of Natural Linoleic Acid in Soybean Oil Hydrogenated with a Copper Catalyst

Iodine value	Composition according to GLC (wt %)					S_L	wt % Natural linoleic acid	% Natural linoleic acid in C_{18} diene
	C_{18} triene	C_{18} diene	C_{18} monoene	C_{18} sat.	C_{16} sat.			
133.5[a]	7.5	51.0	25.5	3.5	11.5	....	50.7	100
111.3	Trace	44.5	39.5	4.0	11.0	~12	34.4	77
112.8	Trace	46.0	38.5	4.0	11.0	~12	39.9	87
114.2	1.0	46.5	37.0	4.0	10.5	10	38.6	83
119.2	2.0	50.0	32.5	3.5	11.5	11	36.4	73

[a] Starting oil.

(<3) quoted in the Introduction for other catalysts. Thus, using a copper catalyst it is possible to reduce the linolenic acid content considerably while maintaining the linoleic acid content on a high level. About 80% of the linoleic acids are still natural linoleic acid.

It follows further from Table II that oleic acid under the conditions mentioned in Table I is not hydrogenated to stearic acid. This means that copper catalysts have absolute selectivity in the conventional concept of selectivity in fat hardening which aims at decreasing the polyunsaturated fatty acid content without formation of stearic acid. It is defined as the ratio of the rate constants of the linoleic and oleic acid hydrogenation ($S_O = k_L/k_O$) in the following scheme:

$$\text{L (diene)} \xrightarrow[k_L]{+H_2} \text{O (monoene)} \xrightarrow[k_O]{+H_2} \text{S (saturated)}$$

Apparently $k_O = 0$ in our experiments; so that copper catalysts have an infinite S_O-value. That it is very high has been known for a long time. Hilditch and Moore (5) in 1923 hydrogenated cottonseed oil with nickel and copper on kieselguhr catalysts and found that the latter were far more selective in regard to the formation of stearic acid. More recently Japanese authors, especially Miyake (11), investigated copper catalysts in the hydrogenation of whale oil and other oils and also found that very high S_O-values can be reached with these catalysts.

Properties of Copper-Hardened Soybean Oil

Storage Stability. To examine the keeping properties of the copper-hardened soybean oil of different I.V., organoleptic tests were made in which the hydrogenated products were compared with the fully refined soybean oil and sunflower-seed oil. Two tests were employed, viz., a so-called quick test, in which the oil is tested during 4 days when placed in diffuse daylight, and a slow test, in which the oil is stored in the dark at a temperature of 15C and tested once every 2 weeks during a period of 6 weeks. The tests were carried out by a skilled taste panel. In the slow test the preferences were expressed; in the quick test the assessment was expressed in figures of merit from 0 to 6. The results of these tests are collected in Table III. From Table III it follows that the stability against flavor reversion of a copper-hardened soybean oil with an I.V. of 112 is considerably higher than that of the original soybean oil. The keeping properties of copper-hardened soybean oil with an I.V. of 115 are about the same as those of sunflower-seed oil.

Melting Behavior. This of course depends strongly on the iodine value of the hardened oil. There is not much difference in melting behavior between a copper and a nickel-hardened soybean oil if both products are compared at the same iodine value and the nickel hardening takes place under optimum selective conditions. On the other hand, when the aim is the production of a satisfactorily keepable oil from soybean oil it is more meaningful to compare both products at the same linolenic acid content, e.g. 1%. On this basis, copper-hardened soybean oil is considerably more liquid than the nickel-hardened product due to the high S_L- and S_O-values of copper catalysts. For example, after winterizing at 5C for 18 hr, the yield of the liquid phase for the copper-hardened soybean oil was 86% and for the nickel-hardened oil 50%.

Comparative Trials with Copper and Nickel Catalysts

In order to demonstrate more clearly the difference between copper and nickel catalysts, comparative hydrogenations on the same starting soybean oil were carried out. Samples were taken at different stages of the hydrogenation, and after filtration and thorough removal of copper traces analyzed for the data given in Table IV.

The content of linolenic acid as a function of the percentage of linoleic acid is plotted in Figure 1.

Some Aspects of the Structure of Copper Catalysts

General

Our studies on the structure of copper catalysts were mainly devoted to the copper catalyst mentioned in the preceding paragraphs (symbol: Cu-Mg-SiO_2 catalyst; grain size: 2 to 10 μ; BET-surface area: in the order of 150 m^2/g catalyst; average pore width: in the order of 50 Å). The selectivity characteristics of this catalyst must be ascribed to the copper part of the catalyst, because such catalysts as copper on alumina, copper on chromia, copper on kieselguhr, etc., also show a very similar selectivity pattern. However, the activity of copper catalysts in fat hardening may vary considerably with the type of carrier and with the method of preparation.

In the literature, opposing views are found on the question whether elementary copper or a copper compound is the active center in a copper catalyst. Therefore the first investigations concerned the state in which the copper is present in the activated catalyst.

TABLE III

Organoleptic Tests of Copper-Hardened Soybean Oil Compared with Unhardened Soybeans Oil and Sunflower-seed oil

Slow test [number of persons preferring fully refined (A) or hydrogenated refined (I.V. 112) soybean oil (B) after 0–6 weeks]

	0 weeks	2 weeks	4 weeks	6 weeks
A	6	0	1	0
B	14	19	19	20

Quick test [assessments of a 10-person panel after 0–4 days for soybean oil: *A*) refined; *B*) hydrogenated refined (I.V. 112); *D*) idem (I.V. 115); and refined sunflower-seed oil *C*)]

	0 days	1 day	2 days	3 days	4 days
A	5+	4−	2½	Very bad	
B	6	6	5½	5−	4½
C	....	6	6	5	....
D	....	6	6	6−	....

TABLE IV

Comparative Hydrogenations at 185C of Soybean Oil Using a Nickel Catalyst at 1 Atmosphere Gauge Pressure H_2 and Copper Catalyst at 5 Atmospheres Gauge Pressure H_2

Catalyst	Iodine value	Composition determined by GLC (wt %)[a]					Wt % *trans* fatty acids	S_L
		C_{18} triene	C_{18} diene	C_{18} monoene	C_{18} sat.	C_{16} sat.		
Ni on guhr (0.1% Ni on oil)	120.9	4.5	44.0	35.0	5.5	11.0	6.5	2.5
	111.4	4.0	37.5	39.5	5.0	12.0	12.0	2.0
	102.2	3.0	32.0	45.0	6.0	12.0	19.5	2.0
	98.5	2.0	28.0	52.5	6.0	11.0	23.0	2.0
	91.7	0.5	23.5	58.0	7.0	11.0	25.5	2.5
Cu on guhr (0.2% Cu on oil)	127.0	5.5	53.0	26.0	4.0	11.5	4.0	8.0
	120.8	2.5	51.5	31.5	3.5	11.0	7.0	8.0
	115.3	1.5	46.5	35.0	4.0	11.0	9.0	7.0
	112.1	0.5	44.5	40.0	4.0	11.0	13.0	8.0
Starting oil	132.3	8.0	52.0	24.0	4.0	11.5	0	

[a] The totals of the fatty-acid composition vary from 98 to 100%. This is due to the fact that the fatty acids $< C_{16}$ and those $> C_{18}$ have been omitted because their analysis is rather inaccurate.

As already mentioned in the hardening procedure, wet activation of the catalyst can take place in the initial stage of the hardening. In this case an induction period is observed before the actual hardening starts. On the other hand, dry activation is possible in a hydrogen stream at a temperature of 150 to 300C, depending on the type of catalyst. When this catalyst is introduced into an oil to be hardened, no induction period is observed. Apparently a reduced form of a copper compound is essential to obtain catalytic activity. Because dry and wet activated catalysts behave very similarly, structure investigations have been carried out using dry activated catalysts.

The State of Copper in Activated Copper Catalysts

In this investigation the presence of elementary copper (0), copper (I) and copper (II) compounds must be considered. X-ray analysis gave little information on this problem, because—as is often the case in the x-ray analysis of catalysts—the diffraction patterns were very vague, which indicates poorly crystallized compounds and/or a small crystallite size.

Also chemically it is rather difficult to differentiate quantitatively between copper (0), copper (I), and copper(II) compounds. As soon as such a system comes into contact with water, the following equilibrium is established:

$$Cu^{2+} + Cu \rightleftarrows 2\ Cu^{+}$$

In a 4 N sulfuric acid solution this equilibrium is shifted to the left, in a 4 N hydrochloric acid solution to the right as a result of the formation of the $CuCl_2^-$ complex. On treating the activated catalyst with sulfuric acid, any copper(I) will therefore be converted into Cu^{2+} ions and copper (0). On the other hand, on treating the activated catalyst with hydrochloric acid, possibly present Cu^{2+} ions will oxidize copper (0) to Cu^+ ions, which will be bound in the $CuCl_2^-$ complex. Hence, separate determination of copper (0), copper (I) and copper (II) is not possible by conventional chemical methods. However, it will be clear that during extraction of activated copper catalysts with appropriate solutions there is no change in the *mean* oxidation state of copper, provided the possibility of oxidation by air is excluded. Therefore, this mean oxidation state of copper, defined as x in the hypothetical formula CuO_x, can be determined by chemical methods. The following method gives very reliable results.

By treatment with a 2 N sulfuric acid solution at room temperature the activated catalyst is disintegrated completely and all copper(I) compounds, if present, are converted into copper (0) and Cu^{2+} ions. Then the resulting suspension is treated with a solution of iron(III) ammonium sulfate at boiling temperature for about 10 min, as a result of which the copper (0) is oxidized to Cu^{2+} ions according to the reaction:

$$Cu + 2\ Fe^{3+} \rightarrow Cu^{2+} + 2\ Fe^{2+}$$

The Fe^{2+} ions formed are titrated with potassium permanganate solution; the % total copper in the catalyst is determined iodometrically after oxidation of the activated catalyst with nitric acid; the value of x is calculated from

$$x = 1 - \frac{\%\text{ copper as calculated from the permanganate titration}}{\%\text{ total copper}}$$

It will be clear that if $x < 0.5$ the catalyst must contain copper (0); at $x = 0.1$ the minimum amount is 80% and the maximum amount is 90% relative to the total copper content. Depending on the total copper and magnesium contents in the catalyst and the activation method applied, x-values ranging from 0.1 to 0.8 were obtained, so it is evident that the active center of copper catalysts consists of, or contains, a reduced form of copper. Taking into account that catalysts with $x = 0.1$ show high activity (see next section), this reduced form probably is copper (0).

In order to obtain more evidence that the presence of copper (0) is essential for catalytic activity, the following method, based on a paper by Ubaldini and

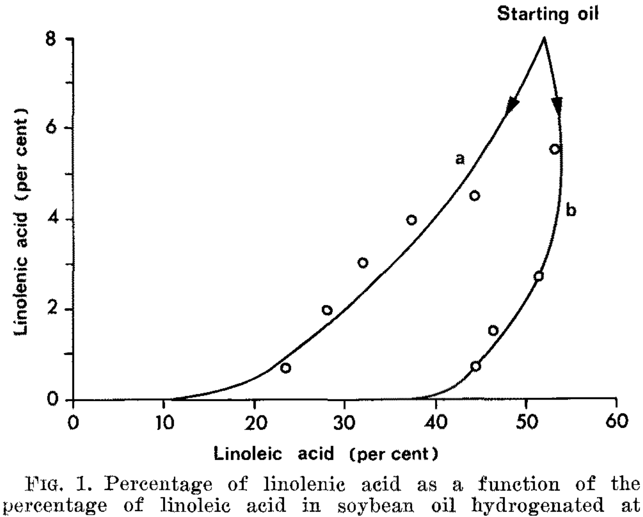

FIG. 1. Percentage of linolenic acid as a function of the percentage of linoleic acid in soybean oil hydrogenated at 185C (a) with nickel catalyst at 1 atmosphere and (b) with copper catalyst at 5 atmospheres gauge pressure H_2.

Guerrieri (21) was developed to determine the amount of copper(0) in activated catalysts.

The activated catalyst is boiled with a solution of sulfur in carbon disulfide by which copper (0) is transformed into copper sulfide, but copper oxides, if present, are not. In this nonaqueous medium no disproportionation of Cu(I) occurs. The solids are filtered off and treated on the filter with a 2 N hydrochloric acid solution. As a result of this treatment only the copper oxides dissolve. The amount of copper in the remaining copper sulfide (which is equal to the amount of copper (0) in the catalyst) is determined iodometrically after dissolution in nitric acid.

The method gave excellent results on model mixtures of copper metal and copper oxides and enables us to determine the amount a of copper (0) relative to the total copper content in activated catalysts. As it appeared that, within the experimental error, $(1-a)$ always equalled x (the mean state of oxidation), the conclusion must be that the reduced form of copper in activated copper catalysts is copper (0), since no measurable amounts of Cu(I) are present.

Relation Between the Mean State of Oxidation of Copper and the Catalytic Activity

In order to study the catalytic properties of copper catalysts more conveniently, vapor phase hydrogenation was applied. This method has the advantage that diffusion limitations can be eliminated, which is hardly possible in liquid phase hydrogenation. In our equipment cyclohexene was hydrogenated over a copper catalyst bed under such conditions that diffusion limitations did not occur. Therefore, the observed rate of hydrogenation to cyclohexane may be considered as a measure of the size of the catalytic surface area.

First of all it appeared that this rate increased with decreasing mean state of oxidation (x) of a certain copper catalyst in the range $x=1$ (rate is zero) to $x=0.35$. So it may be concluded that the decrease in x results in an increase of the catalytically active surface area. This is a further indication that the active center of activated copper catalysts consists of copper metal crystallites; whether these are promoted by the carrier or by traces of other substances to become catalytically active is under investigation.

On the other hand it was observed that in sintering experiments the activities in soybean oil and cyclohexene hydrogenation showed a linear relationship, which indicates that the investigated Cu-Mg-SiO_2 catalyst has a very good accessibility for triglyceride molecules. This may be one of the reasons that Cu-Mg-SiO_2 catalysts have appeared to be very suitable for application in soybean oil hardening.

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