Continuous Hydrogenation of Fats and Fatty Acids at Short Contact Times[1]

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ABSTRACT

Continuous hydrogenation of fats and fatty acids using suspended catalysts was studied in a vertical flow reactor packed with Raschig rings. A short time of reactive contact of the fat or the fatty acid with the catalyst and hydrogen is the unique feature of this system. A nickel catalyst used in the hydrogenation of soybean oil gave a reduction of 40-50 iodine value units per min, small amounts of *trans*-isomers (10-20%), large proportions of linoleate in unreduced octadecadienoyl moieties (70-80%), and nonselective reduction of polyunsaturated acyl moieties (linoleate selectivity ratio 1-3). Another nickel catalyst, used in the hydrogenation of tallow fatty acids, also gave a reduction of 40-50 iodine value units per min and nonselective reduction of polyunsaturated fatty acids. A copper chromite catalyst used in the hydrogenation of soybean oil gave a reduction of 10-15 iodine value units per min, low levels of *trans*-isomers (10-15%), and selective reduction of linolenoyl moieties (linolenate selectivity ratio 4-6). Composition of positional isomers of *cis*- and *trans*-octadecenoyl moieties in partially hydrogenated products obtained both with nickel and copper chromite catalysts reveals that essentially the same mechanisms of isomerization are involved in continuous hydrogenation at short time of reactive contact as in batch hydrogenation.

INTRODUCTION

Catalytic hydrogenation of unsaturated lipids carried out in stirred reactors in a discontinuous manner generally requires considerable periods of time to attain sufficient reduction of the olefinic bonds (1). During the prolonged treatment with hydrogen and the catalyst, several competing reactions apart from saturation of the olefinic bonds are known to occur extensively. They yield large proportions of geometrical and positional isomers of the unsaturated lipids (2).

Continuous hydrogenation of fats using stationary catalysts in a flow reactor has been shown to give high overall rates of reduction of olefinic bonds at a short residence time of the fat in the reactor (3-5). In this system the kinetic patterns of reactions governing the selectivity of hydrogenation of individual unsaturated acyl moieties, as well as the pattern of their isomerization, have been found to be distinctly different from those observed in batch hydrogenation (5).

The present study is an extension of the aforesaid work using suspended catalysts. We have hydrogenated soybean oil and tallow fatty acids in a continuous flow reactor using nickel and copper catalysts in suspension. The unique feature of this system is that the time of reactive contact of the fat or fatty acid with the catalyst and hydrogen is much shorter (1-2 min) than in batch hydrogenation in stirred reactors. Our aim was to determine to what extent the short reaction period in such a system can affect the kinetic pattern of reactions governing selectivity and isomerization.

EXPERIMENTAL PROCEDURES

Material

Refined soybean oil was obtained locally. Distilled tallow fatty acids, type Edenox Ti, were provided by Henkel & Cie, D-4000 Düsseldorf, Germany. All reagents were of analytical grade, obtained from E. Merck AG, D-6100 Darmstadt, Germany.

Nickel catalyst A (containing 23% nickel and 12% kieselguhr in hardened fat), nickel catalyst B (containing 21.5% nickel and 11.5% SiO_2 in hardened fat) and copper chromite catalyst (containing 51% CuO and 47% Cr_2O_3) were all commercial products. Prior to hydrogenation the nickel catalysts A and B were melted and leached with soybean oil and tallow fatty acids, respectively, in order to displace the hardened fat originally present in these catalysts. The copper chromite powder was suspended in soybean oil and reduced to the active catalyst by heating it at 180 C for 30 min while hydrogen was bubbled through the suspension. Subsequently, the catalyst was filtered and leached with soybean oil in order to displace all the partially hydrogenated fat.

Hydrogenation

Continuous hydrogenations were carried out in a laboratory unit similar to the one used earlier (5). A vertical stainless steel tube, internal diameter 40 mm, length 90 cm, served as reactor; it was packed with Raschig rings made of glass, 6 mm by 6 mm. The reactor was adjusted to the desired temperature, ranging from 180-220 C, and hydrogen pressure, ranging from 2-50 atm; the oil or the fatty acids containing various concentrations of the suspended catalyst were preheated and delivered continuously into the reactor from the top at a chosen flow rate between 2-4 l/h. Hydrogenation occurred during the short residence time (40-55 sec) of the liquid reactant containing the suspended catalyst in the bed of Raschig rings. The hydrogenated product emerging from the lower end of the reactor was separated from hydrogen, cooled to 60-70 C and filtered to remove the catalyst. During hydrogenation the pressure in the reactor was maintained by supplying fresh hydrogen. Between two hydrogenations, the reactor was always rinsed with the unhydrogenated oil or fatty acids in order to prevent any deposition of the catalyst on the bed of Raschig rings.

The time of reaction, Δ t, represented by the average residence time of the liquid reactant in the tubular reactor was determined experimentally at various flow rates and temperatures as described earlier (5). The lower end of the reactor was connected to the receiver via a transparent pressure tubing. The reactor was adjusted to the desired temperature and pressure. The preheated oil without the catalyst was then pumped through the reactor for several minutes in order to rinse the bed of Raschig rings. Subsequently, the metering pump, preadjusted to deliver the oil-catalyst-suspension into the reactor, was started, and the time required until the first drop of the dark colored suspension emerged out of the reactor was noted.

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[1] The terms "linoloyl" and "linolenoyl" are used throughout to designate 9-*cis*, 12-*cis*-octadecadienoyl and 9-*cis*, 12-*cis*, 15-*cis*-octadecatrienoyl groups, respectively.

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TABLE I

Continuous Hydrogenation of Soybean Oil Using Nickel Catalyst A.
Effects of Pressure and Catalyst Concentration.
(Temperature 200 C; Flow Rate 2 1/h.)

Run no.	H_2 atm	Catalyst conc. % Ni	Iodine value (IV)	ΔIV/min	trans %	Conjugated dienoates %	Linoleate % of 18:2	Fatty acids % 18:0	18:1	18:2	18:3
Unhydrogenated			134		0.0	0.0		3.7	22.2	55.7	7.2
1	2	0.015	110	27	12.2	1.1	84	8.3	35.4	38.6	5.2
2	6	0.015	96	43	15.3	0.8		16.6	37.1	31.1	4.0
3	11	0.015	87	54	14.1	0.7		22.8	34.5	27.7	3.5
4	2	0.15	83	56	18.1	0.0	76	21.5	40.1	24.2	2.5
5	6	0.15	60	81	17.5			36.0	37.3	13.9	1.3
6	11	0.15	47	94	16.9			43.9	34.5	9.0	0.8
7	2	1.5	78	61	21.1	0.0	57	23.2	41.8	21.4	1.9
8	6	1.5	29	114	15.1	0.0		57.3	28.3	2.9	0.0
9	16	1.5	5	141				82.6	5.4	0.0	0.0

TABLE II

Continuous Hydrogenation of Soybean Oil Using Nickel Catalyst A. Effect of Temperature.
(Catalyst Concentration 1.5% Ni; Hydrogen Pressure 2 atm; Flow Rate 2 1/h.)

Run no.	Temp. C	Iodine value (IV)	ΔIV/min	trans %	Conjugated dienoates %	Linoleate % of 18:2	Fatty acids % 18:0	18:1	18:2	18:3
Unhydrogenated		134		0.0	0.0		3.7	22.2	55.7	7.2
1	185	78	61	17.5	0.0	79	25.0	37.4	23.4	2.2
2	200	78	61	21.1	0.0	57	23.2	41.8	21.4	1.9
3	220	69	71	25.8	0.0	25	25.8	46.1	15.1	1.3

Analytical Methods

All gas chromatographic analyses were carried out in a Perkin-Elmer instrument (F-7) equipped with flame ionization detectors. Quantitative results were obtained using an Autolab System IVb Chromatography Data Analyzer. The starting materials and the hydrogenated products were converted to methyl esters using a mixture of methanol, benzene and sulfuric acid (6). The methyl esters containing little or no conjugated octadecadienoates were analysed at 205 C on a stainless steel column, 2 m by 2 mm, packed with EGSS-X on Gas-Chrom P, 100-120 mesh (Applied Science Laboratories, Inc., State College, Pa. 16801, U.S.A.). Samples containing significant amounts of conjugated methyl octadecadienoates were chromatographed at 200 C on a stainless steel column, 2 m by 2 mm, packed with Silar-5CP on Gas-Chrom Q, 80-100 mesh (Applied Science Laboratories, Inc.).

Iodine values (IV) were calculated from fatty acid composition. The proportion of conjugated octadecadienoyl moieties was determined by UV spectrophotometry (7). The percentage of isolated *trans* double bonds was determined by IR spectroscopy using methyl elaidate as a standard (8). The total content of octadecatrienoyl and octadecadienoyl moieties each having 9-*cis*, 12-*cis* configuration was determined enzymatically using lipoxidase (9). From these values the contents of linolenoyl moiety, determined by gas chromatography, were subtracted to give a close approximation of the level of "natural" linoleoyl moiety.

In order to determine the positional isomers in octadecenoyl moieties, the samples of methyl esters were fractionated into methyl *cis*- and *trans*-octadecenoates by argentation thin layer chromatography (10). The methyl ester fractions were subjected to reductive ozonolysis (11) and the resulting mixtures of aldehydes and aldesters were analyzed by gas chromatography using a column, 2 m by 2 mm, packed with 10% OV-17 on Gas-Chrom Q, 80-100 mesh (WGA, D-4000 Düsseldorf, Germany), coupled with another column, 0.6 m by 2 mm, packed with 3% OV-225 on Supelcoport (Supelco, Inc., Bellefonte, Pa. 16823, U.S.A.); the temperature was programmed from 50 C to 270 C, 5 C/min (12). Quantitative results were obtained by applying response factors for the aldehydes and aldesters (13).

The overall rate of hydrogenation was calculated as rate of decrease in iodine value, ΔIV/Δt and expressed as Δ IV/min. This value is a measure of the overall reaction rate and not a measure of the rate constant. Selectivity of the catalyst was calculated as linoleate selectivity ratio (LSR) and linolenate selectivity ratio (LnSR) from the fatty acid composition of the partially hydrogenated products using established method (14,15).

RESULTS AND DISCUSSION

Some typical results of continuous hydrogenation of soybean oil using the nickel catalyst A at short time of reactive contact are given in Tables I and II.

Table I shows the effects of pressure and catalyst concentration. It is evident that extensive hydrogenation at overall rates as high as 40-50% iodine value units per min is achieved using 0.015% nickel only (runs 1-3). As expected, the overall rate of hydrogenation is greatly increased by increasing both catalyst concentration and hydrogen pressure (runs 1-3, 4-6 and 7-9). Thus, using 1.5% nickel and a pressure of 16 atm (run 9), practically a fully saturated fat is obtained at an overall rate of 141 iodine value units per minute.

Relatively little *trans*-isomers (10-20%) and conjugated octadecadienoyl moieties (<1%) are formed in most experiments. The amount of linoleoyl moieties retained in the hydrogenated product is as high as 84% of the octadecadienoyl moieties (run 1) at a stage where 30% of the octadecadienoyl moieties originally present had been reduced. Even after the reduction of about 55% of the octadecadienoyl moieties (run 4) as much as 76% of the residual octadecadienoyl moieties retain the natural 9-*cis*, 12-*cis* configuration. It seems, therefore, that under the conditions used, most of the unreduced linoleoyl moieties do not undergo positional or geometrical isomerization. A com-

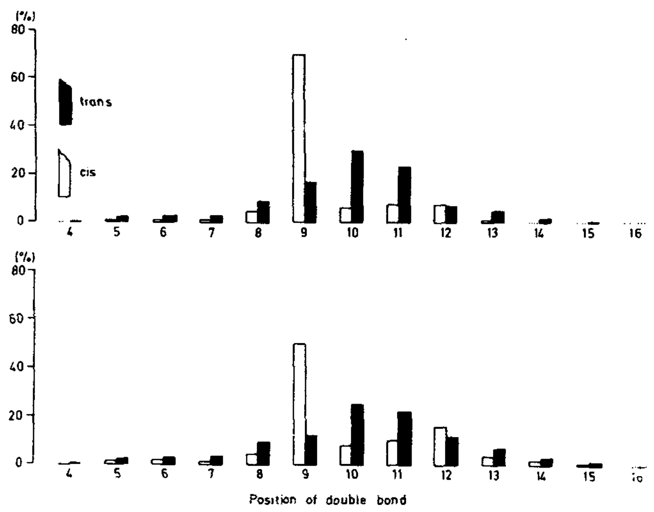

FIG. 1. Distribution of positional isomers in *cis-* and *trans*-octadecenoyl moieties of partially hydrogenated soybean oils obtained with the nickel catalyst A. Samples: Table I, run 4 (top); Table I, run 8 (bottom).

parison of the linoleate contents of the samples from runs 4 and 7 reveals, though, that at the higher catalyst concentration somewhat more isomerization of the unreduced octadecadienoyl moieties occurs. The fatty acid composition of hydrogenated products shows that the hydrogenation of individual polyunsaturated acyl moietics is highly nonselective; linoleate selectivity ratios, LSR, range between 1 to 3 in all runs, compared to 40-50 in corresponding batch hydrogenation (16).

Table II shows the effect of temperature in hydrogenation using the nickel catalyst A. At each of the temperatures studied, the overall rates of hydrogenation achieved are of the order of 60-70 iodine value units per min. At the relatively high catalyst concentration used, the rate of hydrogenation is not influenced by increasing the temperature from 185 to 200 C (runs 1 and 2). At a temperature of 220 C, however, there is some increase in the rate of hydrogenation (run 3).

Somewhat more *trans*-isomers are formed at higher temperatures, as seen in Table II, whereas conjugated octadecadienoyl moieties are not found in any of the products obtained at the three different temperatures. The linoleate content of the hydrogenated products shows that at a temperature of 185 C, as much as 79% of unreduced octadecadienoyl moieties are linoleate (run 1) whereas with increasing temperatures the unreduced octadecadienoyl moieties are extensively isomerized (runs 2 and 3). The fatty acid compositions of the products obtained at each of the three temperatues show, similar to the data given in Table I, that the hydrogenation of the individual polyunsaturated acyl moieties is highly nonselective.

The results given in Tables I and II show in the case of the nickel catalyst three distinct features of continuous hydrogenation at short time of reactive contact compared to batch hydrogenation (16). Under the conditions used, continuous hydrogenation yields only small amounts of geometrical isomers, large proportions of linoleate in unreduced octadecadienoyl moieties, and very low selectivity in the reduction of polyunsaturated acyl moieties over monounsaturated acyl moieties.

Figure 1 shows the distribution of positional isomers in *cis-* and *trans*-octadecenoyl moieties of two products (Table I, runs 4 and 8) obtained with the nickel catalyst A. In the less saturated sample (Table I, run 4), Δ 9-*cis*-octadecenoate is the predominant isomer which constitutes 70% of *cis*-octadecenoyl moieties, followed by Δ11-, Δ12-, Δ10- and Δ8-*cis*-octadecenoates. In the more saturated sample (Table I, run 8), Δ9- and Δ12-*cis*-octadecenoates show pronounced maxima followed by Δ11-, Δ10- and Δ8-*cis*-octadecenoates. The pattern of distribution of positional isomers in *trans*-octadecenoyl moieties is quite similar in the two samples; Δ10- and Δ11-*trans*-octadecenoates predominate apart from considerable amounts of positional isomers ranging from Δ5- to Δ14-*trans*-octadecenoates.

A high level of Δ 9-*cis*-octadecenoate in hydrogenated products can be partly explained by assuming that a major portion of oleoyl moieties originally present in the oil does not undergo isomerization. Moreover, pronounced maxima at Δ9- and Δ12-*cis*-octadecenoates indicate that some of these octadecenoyl moieties might have been derived directly from linoleoyl moieties by 1,2-addition (17). The abundance of Δ10- and Δ11-isomers in *trans*-octadecenoyl moieties reveals that some reduction of linoleoyl moieties to octadecenoyl moieties has occurred via conjugated intermediates (18). The remaining isomers, both in *cis-* and *trans*-octadecenoyl moieties, have probably resulted from positional and geometrical isomerization of octadecenoyl moieties (19). Thus, it seems that in continuous hydrogenation using nickel at short time of reactive contact, essentially the same mechanisms of isomerization are involved as in batch hydrogenation, though the extent of individual reactions is probably different. Lack of selective reduction of polyunsaturated acyl moieties over monounsaturated acyl moieties in continuous hydrogenation can be explained in several ways. The possibility that in continuous hydrogenation the octadecenoyl moieties can effectively compete with the polyunsaturated moieties for the catalyst surface seems rather unlikely, since a competitive chemisorption of octadecenoyl moieties would also imply their extensive isomerization during desorption (20); this does not appear to be the case, as the hydrogenated products contain large proportions of Δ 9-*cis*-octadecenoates. It seems more likely that the conditions employed in continuous hydrogenation at short time of reactive contact favor those reactions which directly yield stearoyl moieties from both linoleoyl and linolenoyl moieties (21).

Some typical results of continuous hydrogenation of soybean oil using the copper chromite catalyst at short time of reactive contact are given in Tables III and IV. Table III shows the effects of temperature and pressure. It is evident that fairly high overall rates of hydrogenation are achieved with copper chromite as well, though the rates are not as high as with nickel. The results of runs 1-3 show that increasing the temperature from 185 C to 200 C increases the overall rate of hydrogenation and formation of *trans*-isomers, but decreases the linolenate selectivity; increasing the temperature to 220 C lowers the overall rate of hydrogenation to some extent, but increases the linolenate selectivity significantly. The results of runs 4 and 5 show that an increase in pressure increases the overall rate of hydrogenation, whereas the linolenate selectivity is practically unaffected by pressure. Under each set of conditions, the linoleate retained in hydrogenated products is as much as 80% of octadecadienoyl moieties.

Table IV shows the effect of concentration of the copper chromite catalyst. At each of the two flow rates studied (runs 1-4), increasing the catalyst concentration from 0.5 to 2.0% decreases the overall rate of hydrogenation. Further increase in catalyst concentration to 5.4% (run 5) does increase the overall rate of hydrogenation compared to that at a level of 2% catalyst. This phenomenon could not be explained. At both flow rates, increasing the catalyst concentration gives higher linolenate selectivity. At both low and high catalyst concentrations (runs 3 and 5), linoleate retained in hydrogenated products is as much as 81% of unreduced octadecadienoyl moieties. The data given in Tables III and IV show that fairly high overall rates of

TABLE III

Continuous Hydrogenation of Soybean Oil Using Copper Chromite Catalyst.
Effects of Temperature and Pressure. (Catalyst Concentration 0.5%; Flow Rate 2 1/h.)

Run no.	Temp. C	H_2 atm	Iodine value (IV)	Δ IV/min	trans %	Conjugated dienoates %	Linoleate % of 18:2	Fatty acids %				LnSR
								18:0	18:1	18:2	18:3	
Unhydrogenated			134		0.0	0.0		3.5	22.1	55.9	6.8	
1	185	6	125	8	9.3	1.9	81	3.5	27.4	53.3	3.3	4.4
2	200	6	123	12	12.4	2.0	81	3.4	30.9	50.0	3.7	3.6
3	220	6	128	6	9.8	1.8	78	3.4	26.8	54.4	3.9	6.0
4	200	6	123	12	12.4	2.0	81	3.4	30.9	50.0	3.7	3.6
5	200	41	115	20	20.5	0.0	77	4.4	36.4	44.9	2.4	3.4

TABLE IV

Continuous Hydrogenation of Soybean Oil Using Copper Chromite Catalyst.
Effect of Catalyst Concentration. (Temperature 185 C; Hydrogen Pressure 6 atm.)

Run no.	Flow rate 1/h	Catalyst conc. %	Iodine value (IV)	Δ IV/min	trans %	Conjugated dienoates %	Linoleate % of 18:2	Fatty acids %				LnSR
								18:0	18:1	18:2	18:3	
Unhydrogenated			134		0.0	0.0		3.5	22.1	55.9	6.8	
1	3.6	0.5	121	15	11.1	2.2		3.5	30.8	50.2	3.0	3.2
2	3.6	2.0	132	3	5.0	1.3		3.5	23.0	55.1	6.1	4.2
3	2.0	0.5	125	8	9.3	1.9	81	3.5	27.4	53.3	3.3	4.4
4	2.0	2.0	132	2	5.5	1.5		3.4	23.2	55.6	6.1	6.0
5	2.0	5.4	128	4	7.3	1.7	81	3.5	24.7	56.0	3.8	6.8
Batch		0.5	111	1	15.8	1.2	61	3.8	41.0	42.5	0.9	4.9

TABLE V

Continuous Hydrogenation of Tallow Fatty Acids Using Nickel Catalyst B.
(Temperature 200 C; Flow Rate 2 1/h)

Run no.	Catalyst conc. % Ni	H_2 atm	Iodine value (IV)	Δ IV/min	Fatty acids %			
					18:0	18:1	18:2	18:3
Unhydrogenated			50		15.5	41.6	6.5	1.0
1	0.025	6	48	2	16.7	41.4	5.6	0.9
2	0.025	11	48	2	16.9	41.4	5.6	0.9
3	0.25	2	40	11	22.1	38.9	2.7	0.6
4	0.25	6	28	25	32.6	30.7	0.5	0.4
5	0.25	11	21	33	41.4	23.5	0.2	0.2
6	0.25	21	14	41	48.3	16.0	0.1	trace
7	0.25	41	10	45	52.5	11.9	0.0	0.0

hydrogenation and linolenate selectivity are attained in the continuous flow system using the copper catalyst at short time of reactive contact. Analytical data of a sample obtained earlier (22) by batch hydrogenation using the same catalyst (Table IV) show a much lower overall rate of hydrogenation, but similar linolenate selectivity. It is interesting to note that in the continuous flow system the proportion of linoleate in unreduced octadecadienoyl moieties is considerably higher than in batch hydrogenation. Since the amount of conjugated octadecadienoates found in hydrogenated products is almost the same in both processes, the differences in the level of linoleate should be due to the presence of nonconjugated octadecadienoate species other than 9-*cis*, 12-*cis*-octadecadienoates. It seems that less of these isomeric octadecadienoate species are formed in continuous hydrogenation at short time of reactive contact than in batch hydrogenation. These isomeric octadecadienoates may, to some extent, be composed of nonconjugatable octadecadienoates derived from linolenoyl moieties (23).

Figure 2 shows the distribution of positional isomers in *cis*- and *trans*-octadecenoyl moieties in the products obtained with copper chromite. The sample from hydrogenation in the continuous flow system (Table III, run 5) and the sample from batch hydrogenation (Table IV) show similar patterns of distribution of positional isomers in both *cis*- and *trans*-octadecenoyl moieties. The *cis*-octadecenoates are almost exclusively composed of the Δ 9-isomer; its level in hydrogenated products reveals that the oleate originally present in the oil does not undergo any isomerization. This is a well known phenomenon with copper chromite catalysts (24). The presence of other isomers in *cis*- and *trans*-octadecenoyl moieties indicates that in both continuous and batch hydrogenation linoleoyl and linolenoyl moieties are reduced via conjugated intermediates followed by 1,2- and 1,4-additions according to known mechanisms (17,23).

It is obvious that in continuous hydrogenation using copper chromite catalyst at short time of reactive contact, essentially the same mechanisms of isomerization are involved as in batch hydrogenation, although the extent of individual reactions is probably different. Moreover, the mechanisms governing selectivity seem to be similar in both processes. It should be noted that in the continuous flow system, the overall rate of hydrogenation with copper chromite is not as high as with nickel. It might be worthwhile to extend this work using more active copper catalysts in order to determine whether at higher overall rates of hydrogenation pronounced differences in the pattern of selectivity and isomerization occur with copper catalysts too.

Some typical results of continuous hydrogenation of tallow fatty acids using the nickel catalyst B at short time of

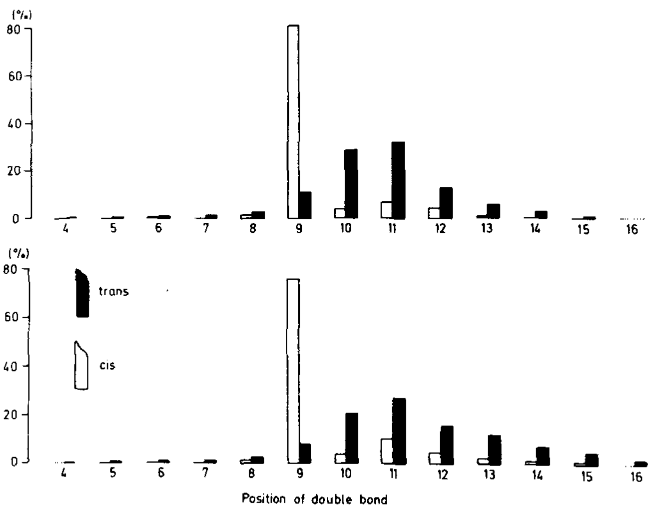

FIG. 2. Distribution of positional isomers in *cis*- and *trans*-octadecenoyl moieties of partially hydrogenated soybean oils obtained with the copper chromite catalyst. Samples: Table III, run 5 (top); Table IV, batch (bottom).

reactive contact are given in Table V. It is apparent that very little hydrogenation occurs at a catalyst concentration of 0.025% nickel. The overall rate of hydrogenation is greatly increased by increasing the catalyst concentration to 0.25% nickel. Increasing the pressure has a very pronounced effect on the rate of hydrogenation. The fatty acid composition of the hydrogenated products reveals no preferential hydrogenation of polyunsaturated fatty acids over monounsaturated fatty acids.

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