Stationary Catalysts for the Continuous Hydrogenation of Fats

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ABSTRACT

Hydrogenation characteristics of a wide variety of stationary catalysts were studied with an aim to explore their possible use in the continuous hydrogenation of fats. Refined soybean oil was hydrogenated continuously in a vertical flow-through reactor over a fixed bed of catalyst. Catalysts investigated were pelleted products containing Raney nickel, reduced nickel, reduced palladium, and copper chromite, as well as granulated alloys of the Raney type, such as Ni-Al, Cu-Al, Pd-Al, and Cu-Cr-Al, which were activated with alkali. These catalysts offered a wide choice of activity, selectivity, and ability to form geometrical isomers. Pelleted copper chromite and granular Raney copper-chromium were found to be highly selective toward the linolenate moiety of soybean oil, whereas pelleted palladium on carrier, as well as granular Raney nickel, Raney copper, and Raney palladium, though moderately selective, exhibited very high activity even at relatively low temperatures. A unique feature of most of the stationary catalysts was the remarkably high rate of hydrogenation. With most catalysts, the iodine value of soybean oil was reduced by 40-60 units within a reaction period of 2-4 min. The hydrogenated fat was practically free of catalyst particles.

INTRODUCTION

Continuous processes have been widely accepted for refining, bleaching, and deodorization of fats; however, catalytic hydrogenation, in the current industrial practice, is mostly a batch process (1).

Some major drawbacks of batch hydrogenation are the problems associated with filtration of the suspended catalyst and possible deleterious effects of prolonged heating on the quality of the hydrogenated fat (2). Continuous processes (3,4) using suspended catalysts do not overcome these drawbacks significantly. Though the period of heating is reduced to some extent, the suspended catalyst has to be filtered before recycling. Apart from the classical Bolton and Lush process (5,6), which was employed earlier with limited success, little effort has been made so far to solve these problems by the use of a fixed bed of stationary catalyst in a continuous operation.

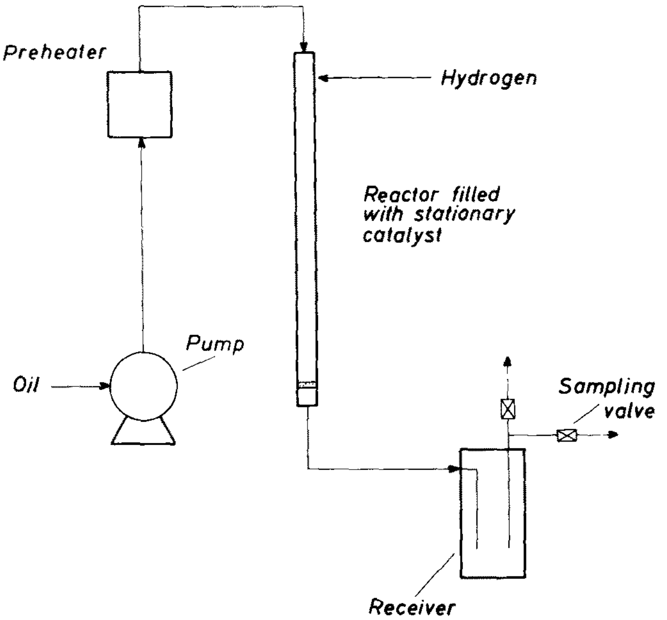

FIG. 1. Apparatus for continuous hydrogenation in a fixed bed reactor.

We have studied the hydrogenation characteristics of several stationary catalysts in a fixed bed with an aim to explore their possible use in a continuous process which should reduce the time of reaction and eliminate filtration. A preliminary account of this work has appeared recently (7). Encouraged by these results, we undertook a detailed study of various pelleted catalysts that are available commercially. Furthermore, we studied the performance of several granulated alloys of the Raney type which were converted to active catalysts by treatment with aqueous sodium hydroxide.

EXPERIMENTAL PROCEDURES

Hydrogenation

Refined soybean oil was used throughout these studies. In several experiments, a solution of the oil in hexane was used. The hydrogenations were carried out in a laboratory unit for continuous reactions, as shown schematically in Figure 1. The vertical tubular reactor (inside diameter 40 mm x 90 cm) was charged with a known amount (generally 1000 cc) of the stationary catalyst and brought to the desired temperature and hydrogen pressure. The oil was preheated and delivered continuously into the reactor from the top at a chosen rate. The oil was hydrogenated during its passage through the bed of catalyst, the product emerging from the lower end of the reactor was collected. During hydrogenation, the pressure in the reactor was maintained by supplying fresh hydrogen.

The processing parameters, such as temperature, hydrogen pressure, and flow rate of the oil were varied to obtain products of desired properties. Liquid hourly space velocity (LHSV) (hr^{-1}) was calculated as the ratio of the flow rate of oil (liters/hr) to the volume of the catalyst bed (liters).

Catalysts

The pelleted catalysts on support, namely Raney nickel, reduced nickel, palladium A (containing 0.5% Pd), palladium B (containing 0.5% Pd, and Cr as promoter), unmodified copper chromite A (53% CuO, 39% Cr_2O_3), modified copper chromite B (36.6% Cu, 32.7% Cr, 6.2% Mn), and modified copper chromite C (containing Ba) were commercial products.

The granulated alloys of the Raney type, namely Raney nickel (Ni:Al, 50:50) and Raney copper (Cu:Al, 50:50) were also commercial products, whereas granulated Raney palladium (Pd:Al, 5:95) and Raney-copper-chromium (Cu:Cr:Al, 4:2:4) were prepared by Degussa Hanau, Hanau, Germany, according to our specifications.

Pelleted Raney nickel, reduced nickel, and the two varieties of palladium were used in the hydrogenations without any prior treatment. The pelleted copper chromite catalysts were activated by various procedures. The unmodified copper chromite A and the modified copper chromite B containing manganese as promoter were activated by reduction with cyclohexanol under reflux for 8 hr. In one set of experiments, the copper chromite B was activated by heating in air at 350 C for 6 hr. The modified copper chromite C, containing barium as promoter, was obtained in a reduced state and was used without any further treatment. This catalyst, according to the manufacturer, had been reduced under hydrogen at 180-200 C and stored under methyl esters derived from hydrogenated coconut oil. Prior to use in hydrogenation, this catalyst was washed repeatedly with refined soybean oil to displace these methyl esters.

Granular Raney nickel, Raney copper, Raney palladium, and Raney copper-chromium were activated by treatment with 20% aqueous sodium hydroxide at 60-70 C for 15 min. The aqueous alkali was separated, and the granular catalyst was washed with water to remove the residual alkali. The water over the catalyst was displaced by methanol, and the latter by n-hexane. Finally, the catalyst surface was impregnated with refined soybean oil, which prevented deactivation by atmospheric oxygen.

Analytical Methods

The starting material and the hydrogenated products were analyzed to determine the extent and selectivity of hydrogenation and isomerization reactions. Iodine values (IV) (8) were determined to measure the extent of hydrogenation. Fatty acid compositions were determined by gas liquid chromatography (GLC) of methyl esters in a Perkin-Elmer instrument (F-7) equipped with hydrogen flame ionization detectors. The methyl esters were analyzed on a 2 m by 2 mm inside diameter stainless steel column packed with 15% diethyleneglycolsuccinate (DEGS) on Anachrom 100-110 mesh (Analabs, North Haven, Conn.). In this system, conjugated octadecadienoates overlapped with nonconjugated octadecatrienoates, whereas the diene-conjugated octadecatrienoates appeared as a separate peak after that of the linolenate (9). The content of octadecadienoates and octadecatrienoates in samples which contained conjugated octadecadienoates was calculated as follows (10).

The total amount of dienoates was estimated by adding up the values of nonconjugated dienoates, determined by GLC, and conjugated dienoates, determined by UV spectrophotometry (11). The content of trienoates was estimated by subtracting the conjugated dienoates, measured by UV spectrophotometry from the area percent of the GLC peak, which was composed of nonconjugated trienoates and conjugated dienoates. Diene-conjugated trienoates, if present, were taken into account while calculating the content of trienoates.

The percentage of isolated *trans* double bonds was determined by IR spectroscopy using methyl elaidate as a standard (12).

Activity of the catalyst, represented by the rate of hydrogenation, was expressed as the rate of decrease of IV/min, $\Delta IV/\Delta t$. The rate of hydrogenation was calculated from the drop in IV and the time of reaction Δt, which corresponded to the time of residence of the oil in the catalyst bed. To determine the residence time, the lower end of the tubular reactor (Fig. 1) was connected to the receiver via a transparent pressure tubing made out of polyethylene. The metering pump, preadjusted to deliver the oil at a definite flow rate into the reactor, was started, and the time required until the first drop of oil emerged out of the reactor was noted. Average values of residence time Δt were determined for a given volume of each catalyst at various temperatures and different flow rates of the oil, ranging from 0.2-3.6 liters/hr.

Selectivity of the catalyst was calculated as linolenate

TABLE I

Continuous Hydrogenation of Soybean Oil Using Pelleted Nickel Catalysts[a]

Catalyst	Temperature C	Pressure kg/cm^2	LHSV hr^{-1}	IV	*trans* %	Conjugated dienoates[b] %	Composition by GLC				$\frac{\Delta IV}{\Delta t\ (min)}$	LnSR
							Trienoates[c] %	Dienoates[d] %	Monoenoates %	Stearate %		
	Unhydrogenated oil			131.5	0.0	0.0	8.2	53.0	23.2	4.1		
Raney	110	2	2.4	113.3	6.4	0.0	6.2	43.4	28.5	9.5	10	1-1.5
nickel	145	2	2.4	105.1	10.6	0.0	5.1	39.3	32.9	12.9	15	1-1.5
on support	145	2	0.8	95.3	17.4	0.0	3.5	32.4	39.4	15.3	10	1-1.5
(6 mm Ø x 6 mm pellets)												
	Unhydrogenated oil			130.8	0.0	0.9	9.1	52.9	22.1	3.9		
Reduced	160	6	0.4	114.5	20.1	0.9	6.6	43.5	31.9	6.4	2	1.5-2
nickel on	190	2	0.4	114.3	12.0	1.4	5.5	43.2	31.4	6.7	3	2-3
support	190	8.5	0.4	106.8	18.8	0.4	3.9	37.9	39.5	6.6	4	1.5-2
(1 mm Ø x 3 mm pellets)												

[a] LHSV = liquid hourly space velocity, IV = iodine value, GLC = gas liquid chromatography, and LnSR = linolenate selectivity ratio.

[b] Determined by UV spectrophotometry.

[c] Includes conjugated dienoates.

[d] Does not include conjugated dienoates.

selectivity ratio (LnSR) using the graphical method suggested by Allen (13).

RESULTS AND DISCUSSION

The results of some typical runs for two types of pelleted nickel catalysts are given in Table I. The results show that even at relatively low temperatures Raney nickel is 3-4 times as active as reduced nickel. Both catalysts are nonselective toward linolenate, as evident from the low values of LnSR and from a significant increase in the level of stearate in the hydrogenated products. Reduced nickel exhibits a slightly higher selectivity than Raney nickel. Under the conditions used, both catalysts yield up to 20% *trans*-isomers, whereas conjugated dienoates are formed with reduced nickel only.

Some typical results obtained with two types of pelleted palladium catalysts are shown in Table II. Both catalysts are highly active. Palladium A is more active than palladium B, even at moderately low temperatures. Under the conditions employed, the rate of IV drop is of the order of 20-40 units/min for palladium A, compared to 10-25 units/min for palladium B. Both catalysts are rather nonselective toward linolenate (LnSR 1-3), palladium B being slightly more selective than palladium A. Relatively large amounts of *trans*-isomers are formed by both catalysts, whereas conjugated dienoates are found only in samples hydrogenated with palladium B.

Lately, copper catalysts have been tested in the batch hydrogenation of soybean oil and reported to be highly selective toward the linolenate moiety (14). We have studied the performance of three stationary copper chromite catalysts in continuous hydrogenation. Table III shows the performance of the unmodified copper chromite A, copper chromite B modified by the addition of manganese, and copper chromite C which contains barium as promoter. The results show that, in continuous hydrogenation, all of the three copper chromite catalysts are far more selective than either nickel or palladium.

Copper chromite A and B are similar with regard to selectivity and isomerization. Both catalysts are selective toward linolenate (LnSR 4-6), and both produce up to ca. 20% *trans*-isomers and up to ca. 1.5% conjugated dienoates under the conditions used. However, these catalysts exhibit rather low activities ($\Delta IV/\Delta t = 2\text{-}5$) compared to pelleted Raney nickel or palladium catalysts.

In one set of experiments, we attempted to improve the activity of copper chromite B by heat-activation as suggested by Moulton and coworkers (15). The results given in Table III show that heat-activation does not alter either the activity or the selectivity of this catalyst.

Among the three types of copper chromite catalysts, copper chromite C, containing barium and activated by reduction under hydrogen, exhibits the highest activity and selectivity. Hydrogenation rates of the order of 5-10 IV units/min and linolenate selectivity ratios between 10-15 are obtained with this catalyst. Copper chromite C yields ca. 5-15% *trans*-isomers and ca. 1-2% conjugated dienoates under the conditions used.

A process for continuous hydrogenation in solvent has been reported earlier from our laboratory (16,17). This process permits the hydrogenation of oils in the miscella resulting from solvent extraction of oilseeds. Within the scope of the present work we have studied the performance of several granular Raney catalysts in the continuous hydrogenation of soybean oil dissolved in hexane.

Some typical results obtained with Raney nickel (Ni:Al, 50:50), Raney copper (Cu:Al, 50:50), and Raney palladium (Pd:Al, 5:95) are summarized in Table IV. It is evident that, even at moderate temperatures, high rates of hydrogenation are obtained with granular Raney nickel and Raney copper catalysts. At higher pressures, the rate of IV

TABLE II

Continuous Hydrogenation of Soybean Oil Using Pelleted Palladium Catalysts[a]

Catalyst	Temperature C	Pressure kg/cm^2	LHSV hr^{-1}	IV	*trans* %	Conjugated dienoates[b] %	Composition by GLC				$\frac{\Delta IV}{\Delta t\ (min)}$	LnSR
							Trienoates[c] %	Dienoates[d] %	Monoenoates %	Stearate %		
	Unhydrogenated oil			131.5	0.0	0.0	8.2	53.0	23.2	4.1		
Palladium A (0.5% Pd/Al$_2$O$_3$, 1 mm Ø x 5 mm pellets)	80	1.25	3.6	110.1	8.0	0.0	5.4	43.4	26.9	12.2	12	1.5-2
	100	3.5	1.4	71.4	28.7	0.0	1.8	21.2	38.5	29.6	19	1-1.5
	165	3.5	3.6	68.5	34.8	0.0	1.3	18.0	40.7	28.6	37	1.5
	Unhydrogenated oil			131.8	0.0	0.0	7.1	57.3	21.9	3.0		
Palladium B (0.5% Pd on support contains Cr as promoter, 5 mm Ø x 3 mm pellets)	150	2	1.0	112.4	15.9	1.2	5.4	49.4	25.7	7.6	5	2-3
	150	11	1.0	90.2	19.9	0.0	3.9	35.9	30.6	17.1	10	1-1.5
	180	2	1.0	110.3	17.6	1.6	5.4	46.0	28.7	7.7	6	2-3
	180	11	1.0	81.7	24.3	0.0	3.4	30.6	31.2	21.3	13	1
	180	2	3.6	109.1	14.2	1.1	5.3	46.6	25.3	10.4	16	2-3
	180	11	3.6	90.5	15.0	0.8	4.6	36.4	25.2	19.7	29	1-1.5

[a] LHSV = liquid hourly space velocity, IV = iodine value, GLC = gas liquid chromatography, and LnSR = linolenate selectivity ratio.

[b] Determined by UV spectrophotometry.

[c] Includes conjugated dienoates.

[d] Does not include conjugated dienoates.

TABLE III

Continuous Hydrogenation of Soybean Oil Using Pelleted Copper Chromite Catalysts[a]

							Composition by GLC					
Catalyst	Temperature C	Pressure kg/cm²	LHSV hr⁻¹	IV	*trans* %	Conjugated dienoates[b] %	Trienoates[c] %	Dienoates[d] %	Monoenoates %	Stearate %	$\frac{\Delta IV}{\Delta t \text{ (min)}}$	LnSR
	Unhydrogenated oil			131.8	0.0	0.0	7.1	57.3	21.9	3.0		
Copper chromite A (unmodified, 5 mm ϕ x 3 mm pellets, reduced with cyclohexanol)	185	4.0	0.48	125.1	6.4	1.2	6.3	54.3	25.8	3.1	1.3	4-6
	185 (I)[e]	6.0	0.48	122.1	10.9	0.8	4.1	53.4	29.6	3.1	1.9	6-8
	185 (II)[e]	11.0	0.48	110.1	21.4	0.7	1.8	44.9	39.8	3.1	2.4	4-6
	Unhydrogenated oil			129.7	0.0	0.0	7.0	57.9	21.8	3.1		
Copper chromite B (modified with Mn, 5 mm ϕ x 3 mm pellets, reduced with cyclohexanol)	160	3.5	0.5	115.1	11.0	1.4	4.1	51.2	30.8	3.6	2.9	6
	160	11.0	0.5	104.1	20.6	0.0	2.4	39.7	43.5	3.8	5.1	2-3
	180	3.5	0.5	112.1	10.2	1.5	4.8	50.9	29.8	4.5	3.5	4-6
	180	11.0	0.5	102.1	15.9	0.9	3.2	46.6	36.9	3.1	5.5	4
	Unhydrogenated oil			134.6	0.0	0.0	7.1	56.4	20.4	3.7		
Copper chromite B (activated by heating for 6 hr at 350 C	155	8.5	0.5	117.2	12.0	0.0	3.4	47.5	32.9	3.7	3.5	3
	180	2.0	0.5	120.5	6.6	1.7	4.8	50.4	28.2	3.7	2.8	4-6
	180	8.5	0.5	109.9	15.7	0.8	2.5	42.0	38.3	3.9	5.0	3-4
	Unhydrogenated oil			132.4	0.0	0.0	6.3	55.4	22.3	4.6		
Copper chromite C (modified with Ba, 4 mm ϕ x 4 mm pellets, reduced under H_2 at 180 C)	180	3.5	0.24	111.1	9.1	1.9	3.2	51.7	27.9	4.6	3.7	~15
	180	6.0	0.24	105.0	13.2	1.3	1.7	45.3	35.7	4.7	4.7	10
	185	3.5	1.35	116.1	4.8	1.3	4.2	52.0	26.0	5.0	7.8	8-10
	185	8.5	1.35	108.0	14.7	1.2	2.7	45.6	34.3	5.0	11.6	~6

[a] LHSV = liquid hourly space velocity, IV = iodine value, GLC = gas liquid chromatography, and LnSR = linolenate selectivity ratio.

[b] Determined by UV spectrophotometry.

[c] Includes conjugated dienoates.

[d] Does not include conjugated dienoates.

[e] I,II = The partially hydrogenated fat from run I was hydrogenated once more under conditions of run II.

TABLE IV

Continuous Hydrogenation of Soybean Oil Dissolved in Hexane (30% Solution) Using Granulated Raney Catalysts[a]

							Composition by *GLC*					
Catalyst	Temperature C	Pressure kg/cm^2	LHSV hr^{-1}	IV	*trans* %	Conjugated dienoates[b] %	Trienoates[c] %	Dienoates[d] %	Monoenoates %	Stearate %	$\frac{\Delta IV}{\Delta t\ (min)}$	LnSR
	Unhydrogenated oil			131.5	0.0	0.0	9.2	55.9	20.9	3.2		
Raney nickel (Ni:Al = 50:50, 8-10 mm granules)	25	7	3.3	120.1	4.8	0.0	7.5	50.8	24.0	6.7	9	1.5
	90	31	3.3	54.8	14.1	0.0	2.0	16.7	26.2	44.9	58	1-1.5
	100	5	7.6	108.4	13.9	0.9	5.8	40.8	31.7	10.9	34	1.5-2
	Unhydrogenated oil			131.5	0.0	0.0	9.2	55.9	20.9	3.2		
Raney copper (Cu:Al = 50:50, 8-10 mm granules)	100	4	4.9	115.2	10.3	0.1	6.8	46.7	28.2	7.1	16	1-1.5
	100	11	4.9	85.6	19.8	0.9	3.5	26.5	39.8	17.3	46	1-1.5
	100	2	2.8	84.9	27.6	2.2	3.6	21.0	50.9	12.5	36	1.5-2
	Unhydrogenated oil			131.5	0.0	0.0	9.2	55.9	20.9	3.2		
Raney palladium (Pd:Al = 5:95, 6 mm granules)	80	9		108.3	9.3	0.0	6.8	43.2	28.9	10.1		<1
	110	1.5		119.9	6.4	0.0	7.8	50.3	24.8	7.0		1.5

[a] LHSV = liquid hourly space velocity, IV = iodine value, GLC = gas liquid chromatography, and LnSR = linolenate selectivity ratio.

[b] Determined by UV spectrophotometry.

[c] Includes conjugated dienoates.

[d] Does not include conjugated dienoates.

TABLE V

Continuous Hydrogenation of Soybean Oil Using Granulated Raney Catalysts[a]

Catalyst	Temperature C	Pressure kg/cm^2	LHSV hr^{-1}	IV	*trans* %	Conjugated dienoates[b] %	Composition by GLC				$\frac{\Delta IV}{\Delta t\ (min)}$	LnSR
							Trienoates[c] %	Dienoates[d] %	Monoenoates %	Stearate %		
Raney nickel (Ni:Al = 50:50, 8-10 mm granules)	Unhydrogenated oil			129.7	0.0	0.0	7.0	57.9	21.8	3.1		
	150	1.5	0.31	111.0	10.5	0.8	4.7	46.5	26.4	10.3	6	2-3
	180	1.5	0.31	108.0	17.3	3.9	4.7	37.4	32.6	10.9	8	4-6
	190	2.0	1.88	108.5	14.8	2.1	4.9	40.8	29.9	11.4	24	2-3
	190	6.0	1.88	96.9							36	
Raney copper (Cu:Al = 50:50, 8-10 mm granules)	Unhydrogenated oil			129.7	0.0	0.0	7.0	57.9	21.8	3.1		
	155	3.5	0.58	108.9	17.8	0.8	3.8	40.7	36.9	6.3	6	1.5-2
	155	6	0.58	103.1	20.8	0.0	3.0	36.1	39.5	8.9	8	1.5
	185	3.5	0.58	104.2	21.0	1.7	2.9	36.0	41.5	7.5	9	3-4
	185	11	0.58	84.3	28.4	0.0	1.5	19.3	44.0	21.4	15	1-1.5
	185	3.5	8.37	117.1	8.2	1.6	5.3	46.9	28.5	6.2	22	2-3
	185	11	8.37	111.6	10.8	0.9	4.7	47.8	29.1	7.2	32	2-3
Raney copper-chromium (Cu:Cr:Al = 4:2:4, 8-10 mm granules)	Unhydrogenated oil			131.8	0.0	0.0	7.1	57.3	21.9	3.0		
	185	3	0.8	125.0	5.1	1.3	5.6	55.7	25.6	3.0	3	10
	185	21	0.8	120.0	11.4	0.0	3.8	53.5	30.8	3.0	6	6

[a] LHSV = liquid hourly space velocity, IV = iodine value, GLC = gas liquid chromatography, and LnSR = linolenate selectivity ratio.

[b] Determined by UV spectrophotometry.

[c] Includes conjugated dienoates.

[d] Does not include conjugated dienoates.

drop is as high as 50-60 units/min for both of these catalysts. Although the rates of hydrogenation could not be determined for the Raney palladium catalyst, since only a small amount of this material was available, the drop in IV indicates that this catalyst, too, is sufficiently active. Low values of LnSR and the formation of large amounts of stearate show that in solvent hydrogenation all three Raney catalysts are nonselective toward the linolenate moiety of soybean oil. Under the conditions used, the formation of *trans*-isomers and conjugated dienoates is highest with Raney copper, followed by Raney nickel and Raney palladium. Thus, the products obtained with Raney copper contain ca. 10-30% *trans*-isomers, compared to ca. 5-15% *trans* with Raney nickel and ca. 5-10% *trans* with Raney palladium. Moreover, conjugated dienoates are formed to an extent of ca. 2% with Raney copper, and ca. 1% with Raney nickel, whereas Raney palladium does not yield products containing conjugated double bonds.

In the following experiments, the performance of granular Raney catalysts has been studied in the hydrogenation of soybean oil without using a solvent. Typical results obtained with Raney nickel (Ni:Al, 50:50), Raney copper (Cu:Al, 50:50), and Raney copper-chromium (Cu:Cr:Al, 4:2:4) are given in Table V. It is apparent that, also in the absence of a solvent, very high rates of hydrogenation are achieved with both Raney nickel and Raney copper; however, the temperatures required to attain such reaction rates are considerably higher than in solvent hydrogenation. At these higher temperatures, both Raney nickel and Raney copper are more selective toward linolenate (LnSR 2-5) than in solvent hydrogenation. Raney copper provides up to ca. 30% *trans*-isomers, compared to ca. 10-15% *trans*-isomers produced by Raney nickel. Both catalysts yield a few percent of conjugated dienoates.

Among the three granular Raney catalysts, Raney copper-chromium exhibits the highest selectivity. This catalyst is comparable to pelleted copper chromite catalysts, both with respect to activity ($\Delta IV/\Delta t$ = 3-6) and selectivity (LnSR 6-10). Under the conditions used, Raney copper-chromium yields small amounts of both *trans*-isomers (5-10%) and conjugated dienoates (0-1.5%).

The catalysts studied so far offer a wide choice of activity, selectivity, and ability to form *trans*-isomers. Thus, pelleted copper chromite and granular Raney copper-chromium are apparently suitable for the production of stable salad oils by selective hydrogenation of the linolenate moiety of vegetable oils, such as soybean oil and "zero-erucic rapeseed oils." On the other hand, pelleted palladium, granular Raney nickel and Raney copper catalysts appear to be suitable for the production of solid or semisolid fats from vegetable oils whose constituent fatty acids are free of linolenic acid. Products of desired chemical and physical properties are obtained by a suitable combination of the processing variables, such as temperature, pressure, and LHSV. Although the effect of these parameters upon the rate and extent of hydrogenation, selectivity, and isomerization was not studied systematically, the data available indicate the following general pattern for all the catalysts studied.

The rate and extent of hydrogenation are increased by increasing either the temperature or the hydrogen pressure. Decrease in LHSV of the oil increases the extent of hydrogenation. Moreover, within the range of flow rates studied, the rate of hydrogenation increases with increasing LHSV, obviously due to better mixing of oil and hydrogen at the catalyst surface caused by increased turbulence of the oil. Selectivity, measured as LnSR and the amount of stearate formed, is improved in most cases by increasing the temperature and decreasing the hydrogen pressure. Most of these findings agree with the results of a previous work (17) in which cottonseed oil was hydrogenated continuously using granular Raney nickel catalyst. However, on the basis of data obtained in the present work, it has not been possible to determine the effect of processing variables upon the formation of *trans*-isomers during hydrogenation.

A striking feature of continuous hydrogenation in a fixed bed reactor is the remarkably high rate of hydrogenation achieved with many of the catalysts. It is obvious that a high concentration of the catalyst in the reaction zone provides such high reaction rates. When pelleted palladium or granular Raney nickel or Raney copper catalysts are used, the IV of soybean oil is reduced by 40-60 units within a reaction period of 1-4 min. The copper chromite catalysts and the Raney copper-chromium are comparatively less active, but even with these catalysts, an IV drop of 20-30 units is accomplished within 2-5 min. In comparison, much lower rates of hydrogenation generally are obtained in the conventional batch process.

The high rate of hydrogenation in the continuous process described here is of great significance, not only with regard to its economy, but also with regard to undesirable side reactions occurring during hydrogenation. It is likely that certain side reactions, for instance those yielding cyclic products (18) or odoriferous carbonyl compounds (2), might be minimized or eliminated altogether due to a remarkably short time of reaction.

All the catalysts tested so far have a good mechanical stability. The hydrogenated products obtained are essentially free of catalyst particles. Therefore, the filtration step can be eliminated in most cases.

The granular Raney catalysts are rather expensive, however, the simple process for their activation and regeneration might justify their use.

Further work is devoted toward long term studies on catalyst life and processes for their regeneration, as well as studies on physical, chemical, and organoleptic properties of hydrogenated fats obtained by the continuous process.

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