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The Hydrogenation of Fatty Oils with Palladium Catalyst. III. Hydrogenation of Fatty Oils for Shortening Stock

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ALMOST ALL of the three billion pounds of hydrogenated edible oils produced annually in the United States are made with nickel. Although it has been known for a long time that palladium is an exceedingly active catalyst for carbon-carbon double bond hydrogenation, this catalyst has enjoyed no popularity in the edible oil field. The principal deterrent to the use of palladium has been economics, but, with the steadily decreasing ratio in the prices of palladium and nickel, palladium hydrogenations have become economically competitive. We set out therefore to find commercially attractive conditions by which palladium catalysts could give products of suitable stability and plasticity for use as shortening stocks.

Shortening stocks require a wide plastic range, which in turn demands a low amount of *trans* isomers. Usually palladium forms more *trans* isomers than nickel so an effort was made to ascertain how processing conditions could be adjusted to control the *trans* content within the desired limits. Proper control of selectivity was much less of a problem for in most experiments the selectivity was more than adequate. Although unsupported nickel is more selective than unsupported palladium, supported palladium has good selectivity with the conditions used in the present work. Palladium is more active and more selective than all other platinum group metal catalysts and was accordingly the platinum metal of choice for this study. Platinum, rhodium, and ruthenium were also examined, but each was inferior to palladium.

Experimental

Laboratory experiments were done in a stainless-steel hydrogenator of one-gallon capacity, provided with good mechanical agitation, a gas-dispersing system, a cooling coil, and an electrically-controlled heating system. Three pounds of oil were used in each experiment. The oils were soybean (iodine number = 127) and cottonseed and a 70/30 mixture (iodine number = 120) of the two. Processing was controlled by refractive index, and analyses of the oils were made by the official methods of the American Oil Chemists' Society. The *trans* content was calculated from the intensity of the 10.36 μ band, measured in a carbon disulfide solution on a Perkin-Elmer Model 21 infrared spectrophotometer, according to the procedure of Swern *et al.* (29), using the recommendations of the Spectroscopy Committee (30). The catalysts were all palladium on high-surface carbon. Catalysts A, F, G, and H were 1%, 5%, 2%, and 0.5% palladium on carbon powder, respectively. Catalysts B, C, D, and E were 1% palladium partially deactivated by silver and bismuth, containing 0.9%, 1.0%, 0.35%, and 0.5% silver and 0.6%, 0.35%, 0.25%, and 0.35% bismuth, respectively. All catalysts were prepared according to the directions given in the first paper (1) of this series except that the amounts of basic bismuth acetate, silver acetate, and palladous chloride were altered as needed to give these percentages.

Catalyst Activity

Palladium is an exceedingly active hydrogenation catalyst, and adequate hydrogen supply to the catalyst surface is a major problem. Some idea of how rapidly hydrogen is depleted from the catalyst surface may be gained from Figure 1. This is a semi-log

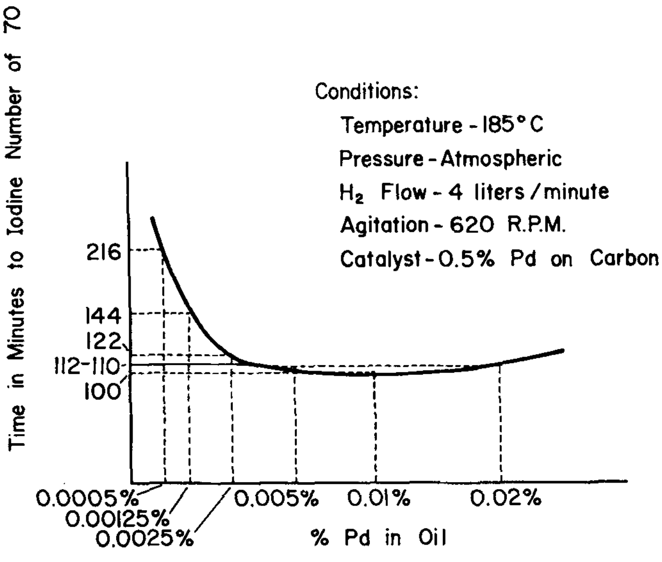

FIG. 1. Hydrogenation rate as a function of catalyst concentration.

plot of the time of processing cottonseed oil to an iodine number of 70 *versus* the concentration of palladium in the oil. Over a wide portion of the plot the time of processing is virtually independent of the amount of palladium, a result best attributed to rate-controlling diffusion of hydrogen from the gas phase through the liquid to the catalyst surface. Even at the lowest concentration of palladium the time of processing does not decrease with increasing amounts of palladium as much as would be expected if sufficient hydrogen were available in the liquid. In Table I these data are calculated as a catalyst-functioning rate, C.F.R., expressed as iodine units reduction per minute per 1% of catalyst. If diffusion were not a rate-controlling factor, the catalyst function rate should be constant as the catalyst concentration is varied.

TABLE I

Effect of Catalyst Concentration on Rate (Figure 1)

Experiment	% Pd. in oil	C.F.R.
1	0.02	18
2	0.01	40
3	0.005	72
4	0.0025	130
5	0.00125	215
6	0.0005	354

Trans Isomer Formation

The *trans* content of a partially hydrogenated oil is dependent in some measure on all the operating variables of the hydrogenation reaction. The following sections give an idea of the direction and magnitude of this dependency.

Agitation. Trans formation is decreasd as agitation is increased. The quantitative relationship between speed of stirring and *trans* formation is shown graphically in Figure 2.

Pressure. Trans formation is decreased as pressure is increased. With other conditions constant, the *trans* content is lowered from 58 to 42% by increasing the pressure from atmospheric to 30 p.s.i.g. The data are given in experiments 15 and 16 of Table II.

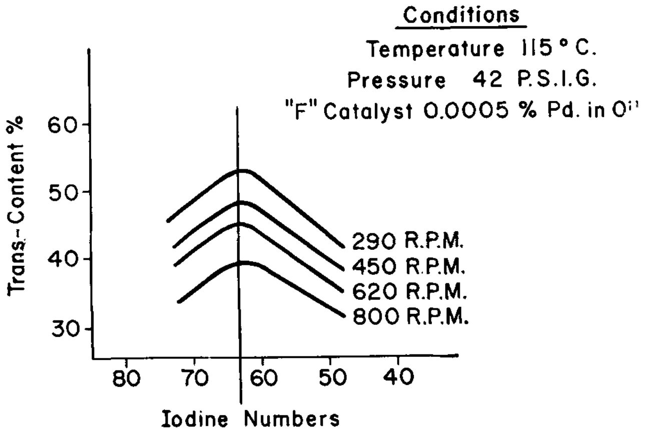

FIG. 2. *Trans* content as a function of agitation.

Temperature. Increasing temperature of reaction gives a higher *trans* content. Experiments 1 and 3 of Table II illustrate this point. At 80°C. the *trans* content was 52.9%, at 42°C. it was only 34.9%.

Catalyst Deactivation. The *trans* content is also dependent on the intrinsic activity of the catalyst. In Experiments 1 and 2 (Table II) the same oil was hydrogenated to essentially the same iodine number under identical conditions except that in 1 an unmodified palladium catalyst was used and, in 2, one which had been deactivated by the addition of silver and bismuth. The more active catalyst gave 52.9% *trans* isomers, the less active only 35.9%.

Concentration of Metal on Carrier. The iso-oleic acids content (2) was found to increase with increasing concentrations of metal on the carrier, but the effect was small (Table III). As the palladium percentage was increased from 0.5 to 5%, the iso-oleic acids content increased from 19.5 to 21.0%. These experiments were made with a constant level of palladium based on oil.

Concentration of Metal in Oil. The iso-oleic acids content (2) is also dependent on the concentration of the metal in the oil and increases as the metal increases. Experiments 1 and 2, Table IV, show that

TABLE II

Laboratory Hydrogenations with Palladium

Ex.	Oil and catalyst		% Pd. in oil	T°C.	Pressure p.s.i.g.	Time, min.	I.N.	Th.N.	Sat. acid, %	Lin. acid, %	*Trans* %	Dilatation			
												21.1°	26.7	36.0	42.0
1	Cottonseed	A	0.02	80	Atm.	255	62.2	59.6	30.3	2.8	52.9	44.0	38.0	9.1	1.0
2	Cottonseed	B	0.02	80	Atm.	340	63.7	61.5	28.3	2.3	35.9	25.1	19.0	4.8	Neg.
3	Cottonseed	A	0.03	42	Atm.	580	64.0	59.6	30.7	5.1	34.9	24.0	18.8	5.1	0.5
4	Cottonseed	C	0.06	42	Atm.	720	63.1	60.0	30.1	3.4	19.5	14.4	11.8	3.6	Neg.
5	Soybean 70 Cottonseed 30	D	0.05	50	Atm.	480	65.8	65.3	22.7	0.1	32.3	21.6	17.1	4.1	Neg.
6	Soybean 70 Cottonseed 30	D	0.02	50	15	108	73.7	66.9	22.4	8.0	22.0	11.2	9.2	3.5	0.3
7	Soybean 70 Cottonseed 30	D	0.02	50	15	120	69.6	65.0	24.4	5.3	24.0	14.9	12.4	5.1	1.1
8	Soybean 70 Cottonseed 30	E Re-used 4 times	0.02	50	30	175	67.1	62.0	28.0	5.9	15.0	20.2	18.5	10.5	5.2
9	Soybean 70 Cottonseed 30	F	0.0005	120	45	100	71.0	64.7	25.0	7.4	35.0	20.4	17.2	7.1	1.7
10	Soybean 70 Cottonseed 30	F Re-used once	0.00065	85	45	95	76.3	66.6	23.1	11.6	23.0	14.7	12.2	5.6	2.0
11	Soybean	F Re-used once	0.00065	85	45	110	77.0	68.3	21.0	10.4	25.0	15.7	13.6	6.4	3.4
12	Soybean 70 Cottonseed 30	A	0.005	60	15	130	68.6	63.9	25.7	5.4	33.2	20.7	16.4	5.2	1.3
13	Soybean 70 Cottonseed 30	A	0.001	75	40	138	70.3	63.1	26.9	8.5	21.2	19.7	17.8	9.8	4.0
14	Soybean	G	0.00045	110	45	150	81.7	74.4	13.8	8.5	39.5	18.2	13.4	3.8	0.9
15	Cottonseed	H	0.001	185	Atm.	......	67.0	......	......	......	58.0	......	......	......	......
16	Cottonseed	H	0.001	185	30	......	66.7	......	......	......	42.0	......	......	......	......

Agitation for experiments 1–13, 800 r.p.m.; 14, 420 r.p.m.; 15–16, 620 r.p.m.
Hydrogen flow rate for experiments at atmospheric pressure = 4 liters/minute.

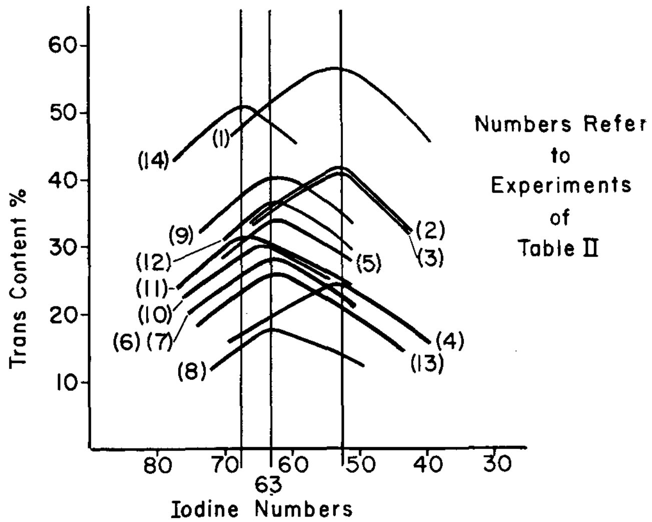

FIG. 3. Variation of *trans* content with feed and conditions.

the iso-oleic acids content is raised slightly from 19.5 to 20.9% when the metal, based on oil, is raised from 0.001 to 0.005%.

Type of Feed. The type of feed is also a factor in determining the *trans* isomers in the product. Soybean oil forms more *trans* isomers than cottonseed oil. The maximum *trans* content occurs at about an iodine number of 70–65 for soybean oil, at 55–50 for cottonseed oil, and at an arithmetic mean for mixtures of the two as shown in Figure III. Presumably the more unsaturated oil will always give more *trans* isomers if the olefins are of similar type. The results are in agreement, in general, with previous investigations (26).

Selectivity

The selectivity achieved in hydrogenation of oils with multiple unsaturation also depends on the operating variables. In general, conditions which favor increased selectivity favor increased *trans* isomer content in the range examined here except, notably, controlled specific deactivation of the catalyst.

Selectivity is improved by catalyst deactivation, Experiments 1, 2, 3, and 4, of Table II. This finding is in agreement with much previous experience with palladium and especially with nickel (1, 3–14). However the contrary opinion also exists, especially in regards to processing with nickel (15–18). Generalities concerning the influence of processing conditions on selectivity must be made with reservation and confined to a relatively narrow set of conditions. For example, increasing the concentration of metal in the oil may increase selectivity (17, 19–21) or decrease it (22–24). In this work increasing the concentration of metal in the oil decreased selectivity, as shown in Table IV. Increasing the concentration of metal on the carrier also decreased selectivity (Table III). Increasing agitation may increase selectivity (24, 25) or decrease it (15–17, 21). In this work increasing temperature increased selectivity, as is generally the case in oil hydrogenation, but increasing temperature has also been observed to decrease selectivity (27, 28). However the influence of conditions on selectivity, with palladium catalysts, is predominately an academic problem for with the conditions employed in this work the selectivity was usually adequate.

TABLE III
Influence of % Pd. on Carrier on Hydrogenation of Cottonseed Oil

Ex.	Catalyst	Total product I.N.	Fatty Acids of Hydrogenated Oil					
			Solid fatty acids, %	I.N. of solid fatty acids	I.N. of total fatty acids	Iso-oleic acids, %	Saturated acids, %	Linoleic acid, %
1	0.5% Pd./C.	67.0	43.8	40.1	70.1	19.5	24.3	2.2
2	1% Pd./C.	67.5	44.5	40.4	70.6	20.0	24.5	3.0
3	5% Pd./C.	66.5	48.3	39.1	69.6	21.0	27.3	4.6

185°C.; atmospheric pressure; 620 r.p.m.; 4 liters H_2/min.; 0.001% Pd. in oil.

TABLE IV
Influence of % Pd. in Oil on Hydrogenation of Cottonseed Oil

Ex.	% Pd. in oil	Total product I.N.	Solid fatty acids, %	I.N. of solid fatty acids	I.N. of total fatty acids	Iso-oleic acids, %	Saturated acids, %	Linoleic acid, %
1	0.001	67.0	43.8	40.1	70.1	19.5	24.3	2.2
2	0.005	66.9	46.9	40.1	70.3	20.9	26.0	4.1

185°C.; atmospheric pressure; 620 r.p.m.; 4 liters H_2/min.; 0.5% Pd. on carbon.

Discussion

The *trans* content of a partially hydrogenated oil was shown to vary with operating conditions of the process and activity of the catalyst. The *trans* content may be linked to these variables in much the same way that Bailey (15) linked these variables to the selectivity of hydrogenation. Agitation, pressure, catalyst concentration, etc., are considered to control selectivity and *trans* content only in that they influence the transport of hydrogen from the gas through the liquid to the catalyst surface. For hydrogen transport rates to have any effect on *trans* content it is necessary that isomerization of *cis* to *trans* have a different dependence on hydrogen concentration than hydrogenation of the double bond. The present data relating *trans* content to processing variables are entirely explicable on the assumption that isomerization has a lower order dependence on hydrogen than does hydrogenation. The greater the deficiency of hydrogen at the catalyst surface, the more hydrogenation will be retarded relative to isomerization.

Trans formation with palladium catalysts becomes a problem then because of the very high intrinsic rate of hydrogenation and consequent depletion of hydrogen on the catalyst surface. Increased agitation diminishes *trans* formation by keeping the catalyst more adequately supplied with hydrogen.

The effect of temperature on *trans* content can also be interpreted in terms of hydrogen supply to the catalyst. With increasing temperature, hydrogenation proceeds faster so if other conditions are constant, the catalyst will have a lower concentration of hydrogen at its surface. Increasing temperatures of reaction should, and do, give a higher *trans* content. The *trans* content also would be increased with temperature if the activation energy for isomerization were higher than the activation energy for hydrogenation. However no estimate can be made of the activation energies from the present data.

The observed dependence of *trans* content on intrinsic catalyst activity or on deliberately deactivated catalysts may be interpreted on a purely physical basis, using the assumption that isomerization has a lower order dependence on hydrogen than hydrogenation. The greater the hydrogen depletion at the catalyst surface, the more isomerization will be favored relative to hydrogenation. Excessive *trans* formation with very active catalysts can be overcome therefore by adequate agitation.

Agitation must be increased with increasing concentration of metal in oil if the *trans* content is to be held constant. Increasing the catalyst concentration merely divides the available hydrogen so that the concentration at the surface of the catalyst is less and *trans* formation is consequently favored.

By proper choice of conditions a shortening stock of good stability and plastic properties may be obtained from hydrogenation with palladium catalysts. The dilation figures obtained for the products from Experiments 4, 7, 10, and 11 show these all to have good plastic properties. These products were obtained with mild operating conditions that would be commercially attractive. The amount of catalysts used in most laboratory experiments was very small so it was difficult to recover them quantitatively and examine their behavior on repeated re-use.

In pilot plant experiments, undertaken to demonstrate that palladium could be used successfully with larger amounts of oil, the amount of catalyst used was larger, allowing it to be recovered and re-used. The results of this work will be reported later, but it may be said now that the products of the laboratory could be duplicated with amounts of catalyst that would be economically attractive.

Summary

Palladium-on-carbon catalysts are exceedingly active for the hydrogenation of natural unsaturated oils when very mild conditions are used. Selectivity is usually good, and *trans* content can be adequately controlled by the proper choice of conditions. In the range of operating variables used in this work, *trans* formation is lessened with increased agitation and pressure, decreased catalyst activity, decreased concentration of metal in oil and on carrier, and with decreased temperature. Some shortening stocks were obtained which have good physical properties, as expressed by their dilatometric curves.

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Isolation of an Hydroxy Acid Concentrate from Wool Wax Acids[1]

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THE PRESENCE of hydroxy acids in the saponifiable fraction of wool wax has been reported by a number of investigators (1, 5, 6, 7, 8, 9, 10, 13). Kuwata (8) used a combination of extraction and distillation to isolate 2-hydroxyhexadecanoic acid. Weitkamp (13) obtained the same acid and 2-hydroxytetradecanoic acid by an amplified distillation of their methyl esters. Horn and coworkers (6, 10), using a countercurrent distribution technique, obtained a 2-hydroxy acid fraction consisting of 27% of the total saponifiable fraction. The latter authors isolated 2-hydroxydodecanoic, 2-hydroxyoctadecanoic, and 2-hydroxy-16-methyl heptadecanoic as well as those acids previously reported.

Other positional isomers of the 2-hydroxy acids that have been isolated are 30-hydroxytriacontanoic acid and 32-hydroxydotriacontanoic acid (7).

In order to study the chemical and physical properties of the hydroxy and unhydroxylated acids, particu-

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