

The Hydrogenation of Fatty Oils with Palladium Catalyst.

IV. Pilot-Plant Preparation of Shortening Stocks

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IN A PREVIOUS PAPER (1) of this series (1-3) laboratory experiments in hydrogenation by palladium catalysts of fatty oils for shortening stocks were described. The effect of operating variables on the selectivity and activity of hydrogenation, especially on *trans* formation, was examined; and by proper control of conditions commercially acceptable shortening stocks were made. However the amount of catalyst used in the laboratory experiments was so very small, it was not possible to recover sufficient catalyst for repeated re-use and so evaluate the economics of the process, or to examine the effect of declining activity on the quality of the product.

We therefore hydrogenated fatty oils to shortening stocks with palladium catalysts in our pilot-plant reactor, where a much better recovery of catalyst was possible. The results of these experiments are described in this paper, and a comparison with results obtained in the laboratory is made.

Experimental

Procedure. Hydrogenations were done in a steam-jacketed, 50-gal. stainless steel reactor. The mixing equipment consisted of a high-speed turbine type of agitator plus a pump which circulated both the oil and catalyst and sprayed them through nozzles at the top of the reactor. Such a system allowed intimate mixing of the oil, catalyst, and hydrogen. In Experiment 1, Table I, 30 g. of carbon powder were added before processing to remove catalyst poisons; in the other experiments no carbon was added. After charging with oil and catalyst the reactor was twice evacuated and twice filled with nitrogen. The oxygen level, as determined by a Deoxo indicator (4), was then about 0.15 to 0.20%. The nitrogen was replaced by hydrogen; and heating, stirring, and

circulation of oil with catalyst were started. The desired operating temperature was reached in 5 to 10 min. Processing was controlled by determination of the refractive index at 45°C. of withdrawn samples. Filtration, after purging with nitrogen, of 50 kg. of oil through cloth and filter paper took 15 to 20 min. The filtered oil contained no particles of catalyst and was completely clear.

Palladium in the used catalyst recharged to the reactor was assayed as follows. About 2.0 g. of accurately weighed oil-soaked catalyst were fired at 750°C., and the residue was moistened with formic acid, dissolved in 5 ml. of *aqua regia*, and filtered. The filtrate was diluted to 300 ml. with water and 25 ml. of concentrated hydrochloric acid. Potassium iodide was added to the solution to precipitate palladium iodide. The precipitate was removed by filtration, washed with hot water, transferred to a crucible, dried at 100°C., and decomposed at 300°C. Finally the residue was heated to 550°C. The palladium oxide film was reduced with formic acid and dried at 125°C. The palladium was weighed.

Analysis of the products obtained in the work were made by the Official Methods of the American Oil Chemists' Society (5). The *trans* content was determined from the infrared absorption of a carbon disulfide solution in a Perkin-Elmer Model 21 infrared spectrophotometer according to the procedure of Swern (6), using the recommendations of the Spectroscopy Committee (7).

Materials. Catalysts F and G were 5% and 2% palladium on carbon powder, respectively. The preparation of the catalysts was described in the first paper of this series (2). The refined, starting soybean oil had an iodine number of 127; the 70/30 mixture of soybean and cottonseed had an iodine number of 120.

TABLE I
Pilot-Plant Hydrogenations with Palladium

Ex.	Oil kg.	Catalyst	% Pd in oil	°C.	Press. p.s.i.g.	H ₂ Ft ³	Time min.	Hydrogenated oil						
								I.N.	Th. N	% Lino-leic acid	% Satur. acid	% <i>Trans</i>	Wiley M.P.	Cong. point
1a	Soybean	F 7.4 g.	0.00062	80	44-	135	110	78.5	68.8	11.6	20.5	25.0	44.5
1b	60 kg.			81	45		125	75.6	66.8	10.5	22.8	27.8	47.1	31.8
2	Soybean	F re-used from Ex. 1	0.00065	81	45	110	260	83	72	13.3	16.9	27	41	24.8
3	Soybean	F re-used from Ex. 2 + 1.88 g. fresh	0.001	80	45	110	280	80.1	69.3	13.0	20.0	27.5	45.2	31.3
4	Soybean	F 6.5 g. fresh	0.00055	82	47	125	220	79.4	69.0	12.4	20.3	25.0	39.2	25.0
	42 kg. Cottonseed													
	18 kg.													
5	Soybean	G 12.4 g. fresh	0.00049	108-114	38-46	120	45	75.7	68.2	8.9	20.9	34.5	42.8	28.2
6a	Soybean	G re-used from Ex. 5	0.0005	107-114	43-47	110	60	82.5	72.4	12.0	16.4	33.7	41.4	24.6
6b	45 kg.						70	79.5	70.0	11.3	19.1	35.0	43.0	27.9
7	Soybean	G re-used from Ex. 6	0.00055	104-121	45	100	75	74.2	67.3	8.1	22.0	36.5	46.6	31.0

Agitation 420 r.p.m. + spray nozzle.
Starting material: soybean I.N. = 127
70/30 mixture of soybean and cottonseed, I.N. = 120.

Results

The conditions and results of the pilot-plant hydrogenation are given in Table I. As is frequently true, they differ somewhat from the laboratory experiments made with supposedly the same operating conditions (compare Experiments 10, 11, and 14, reference 1, with Experiments 4, 1-3, and 5-7 of this paper). The chief reason for the difference probably lies in a different kind and degree of agitation which has been shown to effect both *trans* formation and selectivity (1, 8).

Activity. The time of processing in the pilot plant was generally satisfactory. With re-used catalyst processing the time increased, especially at lower temperatures, but the time decreased sharply as the temperature was raised (Experiments 5-7). Palladium is exceedingly active for the hydrogenation of double bonds, and the amount of metal needed is actually very small. Experiments 1-3 used the same catalyst plus a little fresh catalyst for the third run. The weight ratio of palladium to oil for these three combined experiments was 1:357,000. For Experiments 5-7 combined, using 2% Pd/C, this ratio was 1:545,000.

Selectivity. The selectivity of processing in the pilot plant was satisfactory although it was higher in the laboratory, especially at higher temperatures. Catalyst activity declined with repeated re-use of the catalyst, but the selectivity remained relatively constant. Experiments 5 and 7 illustrate this point.

Trans Content. The *trans* content of all pilot-plant samples hydrogenated at 80°C. was in the range of 25-28%, somewhat higher than obtained in the laboratory. The *trans* content is increased as the operating temperature is increased, but the rate of increase is lower than observed in the laboratory experiments (1).

Dilatation. Figure 1 gives the dilatation curves for stocks made with palladium at 80°C. (Experiments 1-4) and at 110°C. (Experiments 5-7). A typical curve for a commercial stock processed by nickel at 120°C. and 45 p.s.i.g. is given for comparison. The slope of the dilatometric curves increases as the temperature of processing increases, *i.e.*, processing at 110°C. affords a stock with a higher solid fat index at 21.1°C. and lower solid fat index at 42°C. than those obtained by processing at 80°C. if other conditions are the same.

Finished Shortening. To provide a comparison of the products obtained in our pilot plant with those produced commercially with Ni-catalyst, various amounts of "stearine" (highly hydrogenated oil, iodine number = 7, M.P. = 61°C.) were added to our

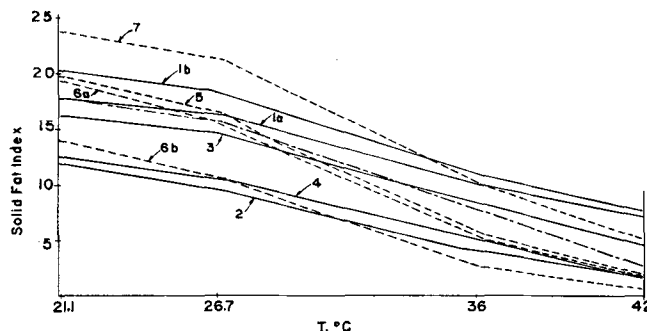


FIG. 1. Dilatometric curves of shortening stocks.

— made with 5% Pd on C, T = 80-82°C.
 - - - made with 2% Pd on C, T = 110°C.
 . . . made with Ni-catalyst, T = 120°C.

stocks. The properties of these shortenings, together with those of five commercial products, are given in Table II. The first sample contains no added stearine since the product obtained directly from the hydrogenation had the properties of a finished shortening.

In general, the shortenings made by palladium hydrogenation differ from market shortenings in that they have a slightly higher iodine number, a little more linoleic acid and more *trans* acids, and somewhat fewer saturated acids. The dilatometric curves of these shortenings are a little higher at 36° and 42°C. and a little lower at 21.1° and 26.7°C. than commercial products, meaning that they have a somewhat wider plastic range. The shortenings made with 2% palladium on carbon have a dilatometric curve more nearly that of commercial products than do the ones made with 5% palladium.

Baking Tests. Three pounds of shortening six months old, from a composite of the pilot-plant experiments, was deodorized in four hours at 210°C. under an absolute pressure of 2 mm Hg. This is less than the time usually required for stocks from nickel hydrogenation, even when deodorized soon after processing. The taste and odor of the sample was good.

To afford an adequate comparison between palladium catalyst shortening and a commercial shortening, both were converted to liquid, tempered, and crystallized by stirring for 10 min. at 10°C., then held at 30-32°C. for 24 hrs., according to the procedure of Steffen and Vander Wal (9). These shortenings were then used in a cake-baking test, 1 hr., 370°F. (9).

Shortening	Weight of cake	Volume of cake	Pound-cake volume values
Commercial	1340 g.	2994 ml.	223
Engelhard	1336 g.	3313 ml.	248

TABLE II
Comparison of Shortenings

Shortening	I.N.	% Linoleic acid	% Saturated acid	% Trans	Congeal point	Dilatation			
						21.1°	26.7°	36.0°	42.0°
No. 1b ^a	75.6	10.5	22.8	27.8	31.8	20.4	18.5	11.5	7.6
No. 2 ^a + 6% stearine.....	78.5	12.4	21.2	25.5	31.3	17.9	16.4	11.3	7.5
No. 3 ^a + 1% stearine.....	79.3	12.7	20.7	27.2	31.5	18.8	17.7	11.5	7.9
No. 4 ^a + 6% stearine.....	75.0	11.5	24.5	23.0	31.4	18.8	17.4	11.6	7.8
No. 6 ^a + 6% stearine.....	77.7	11.0	20.8	31.2	30.0	19.8	18.2	11.0	6.9
Average.....	77.2	11.6	22.1	26.9	31.2	19.1	17.7	11.4	7.5
Commercial A.....	67.7	10.8	32.2	16.0	33.2	22.6	20.3	12.5	7.6
Commercial B.....	75.7	9.1	21.2	27.0	30.9	17.8	16.5	9.5	5.5
Commercial C.....	75.0	9.4	22.3	26.5	31.2	18.3	17.2	10.7	6.1
Commercial D.....	74.0	11.5	25.6	26.4	31.6	20.7	18.9	10.2	6.0
Commercial E.....	75.7	12.0	24.2	26.1	30.5	18.8	17.2	9.7	5.7
Average.....	73.7	10.6	25.1	24.4	31.5	19.6	18.0	10.5	6.2

^a From Table I.

The literature gives pound-cake volume values of around 250 as being the best obtainable. The cake baked with palladium catalyst shortening had a finer texture. This shortening was tested by official Federal Standards for iodine number, acidity, stability, moisture, and smoke point (10). It was satisfactory in all tests.

Summary

Shortening stocks obtained in the pilot plant differ slightly from those obtained in the laboratory under nominally the same conditions. Pilot-plant processing is easily controlled to give a commercially attractive shortening at a cost competitive with nickel. By repeated re-use 1 g. of 5% palladium on carbon catalyst will hydrogenate about 18 kg. of oil to a satisfactory product, and 1 g. of 2% palladium on carbon catalyst about 11 kg. of oil.

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Vinyl Ketostearates. Preparation, Properties, Infrared Spectra, and Analysis of 4- and 12-Ketostearates¹

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THE PREPARATION of vinyl 4- and 12-ketostearates was undertaken to provide monomers for polymerization and copolymerization investigations, to determine the potential utility of vinyl keto esters as internal plasticizers, and to study the effect of the position of the keto group. Polymerization studies will be reported elsewhere.

Vinyl esters of long-chain fatty acids have generally been prepared either by reacting an excess of vinyl acetate with the fatty acid in the presence of a mercuric sulfate catalyst or by vinylation of the fatty acid with acetylene in the presence of zinc salts (5, 10). 12-Ketostearic and 4-ketostearic acids, which have previously been reported (2), were vinyolated with vinyl acetate according to the general procedure of Adelman (1).

The infrared spectra of methyl 4-ketostearate, methyl 12-ketostearate, 4-ketostearic acid, 12-ketostearic acid, vinyl 4-ketostearate, vinyl 12-ketostearate, and the γ -lactone of 4-hydroxy-2-octadecenoic acid were determined in carbon tetrachloride solutions. The absorption bands in the 5.6 micron region (characteristic of the lactone-carbonyl), 5.7 micron region (characteristic of the ester-carbonyl), 5.8 micron region (characteristic of ketone-carbonyl), and 6.1 micron region (characteristic of the vinyl group) were studied and used as a basis for quantitative determination of these groups.

Experimental

Materials. Commercial methyl 12-hydroxystearate obtained from hydrogenated castor oil, Brazilian oiticica oil (*ca.* 56% conjugated triene, calculated as eleostearic acid), Eastman's p-dioxane and practical grade vinyl acetate (freshly distilled), Merck's reagent grade mercuric acetate, Girdler's supported-type (electrolytically precipitated, dry-reduced) nickel catalyst, Baker's reagent grade sodium acetate, chromium trioxide, sulfuric acid, potassium carbonate, glacial acetic acid, methanol, petroleum ether (b.p. 30-60°C.) and acetone, and Johns-Manville's analytical filter-aid (Celite) were used.

Methyl 12-Ketostearate. Commercial methyl 12-hydroxystearate was fractionally distilled under high vacuum. Distillate fractions (b.p. 191°C./0.3 mm., m.p. 54.5-55.4°C.) were oxidized with chromic acid by the general procedure of Rockett (17). To a 5-liter flask, equipped with a mechanical stirrer, a thermometer, and a dropping funnel, were added with stirring 660 ml. of glacial acetic acid and 314 g. (1 mole) of methyl 12-hydroxystearate. The temperature was maintained between 30 and 32°C. while adding dropwise, with stirring, a solution of chromic acid (92 g. of chromic acid, 67 ml. of water, and 1320 ml. of glacial acetic acid) in about 2 hrs. The temperature was maintained between 35 and 40°C. for 90 min. The mixture was poured into 5 liters of water contained in a separatory funnel. After shaking the mixture gently and allowing it to stand for a few hrs., the aqueous layer was drained off. The ester layer was heated to boiling in 3 liters of 6 N hydrochloric acid for 10 min. After siphoning out the aqueous layer, the ester was again heated in 1 liter of 6 N hydrochloric acid for 10 min. The ester was washed twice

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