

Some Factors Affecting Hydrogenation of Milk Fat¹

LLOYD M. SMITH and ANDRES VASCONCELLOS, Department of Food Science and Technology, University of California, Davis, California 95616

ABSTRACT

Hydrogenation of milk fat with palladium and nickel as catalysts was studied at various temperatures, pressures, and concentrations of catalyst. Samples were removed from the laboratory hydrogenator at intervals during the reaction, and changes in refractive index, iodine value, Wiley mp, and percentages of fatty acids and *trans*-isomers were determined. Palladium was several times more active as a catalyst than nickel. Milk fat with an iodine value of 35 and mp of 34 C was hydrogenated with 0.05% palladium to an iodine value of 6 and a mp of 46 C in 30 min at 66 C and 53 psi of hydrogen. Kinetic data for each catalyst yielded two slopes, indicating that a change in reaction rate occurred.

INTRODUCTION

Hydrogenation is used widely to improve the plastic properties, oxidative stability, and color of naturally occurring vegetable oils and fats (1). Partial hydrogenation is particularly important to reduce iodine values to the 60-80 range for margarine and shortenings and to the 110-130 range for salad and cooking oils. Animal fats, such as edible tallow and lard, seldom are hydrogenated except to a slight degree to provide better plastic, working, and shelf-life properties when used for household, bakery, or confectionery products.

Trace hydrogenation has been investigated by Weihe and Mucha (2), Mukherjea, et al., (3) and Vasishtha et al., (4,5) as a means to improve the keeping quality of anhydrous milk fat. In the only report available on more complete catalytic hydrogenation of milk fat, Yoncoskie, et al., (6) described changes in the thermal and optical properties of milk fat hydrogenated to near zero IV. Samples of their hydrogenated milk fats inhibited the fat bloom defect in

dark chocolate (7).

To increase the use of milk fat in food products, there is need to provide fractions with a wider range of physical and chemical properties than those due to normal seasonal and feed variations. Of particular interest would be the use of fractions with improved functional properties in specialty products, such as coffee and cereal creams, sour creams and dressings, frozen desserts, whipped toppings, tropical spreads, chip dips, coatings for ice cream and candies, specialized shortenings, and snack foods. Many of these products would require the availability of milk fat fractions with better resistance to oxidative deterioration and different melting or emulsifying characteristics. Sherbon (8) has reviewed a number of crystallization and fractionation procedures to prepare milk fat fractions on a commercial scale. Hydrogenation might afford an alternative method to crystallization techniques for supplying harder milk fats for specialty uses.

EXPERIMENTAL PROCEDURES

Materials

Milk fat was prepared by melting fresh, unsalted butter at 60 C, washing the fat three times with water at 85 C, and then centrifuging to remove the water. The catalysts used were Nysel flake catalyst Ni-3201 F (Harshaw Chemical, Cleveland, Ohio) containing 30% nickel and 5% palladium on calcium carbonate (Matheson, Coleman and Bell, Norwood, Ohio).

Hydrogenation Procedure

Hydrogenations were done in a custom built apparatus of 1.5 liter capacity (Fig. 1) designed by Smith and Vasconcellos (9). For each experiment, 500 g milk fat plus

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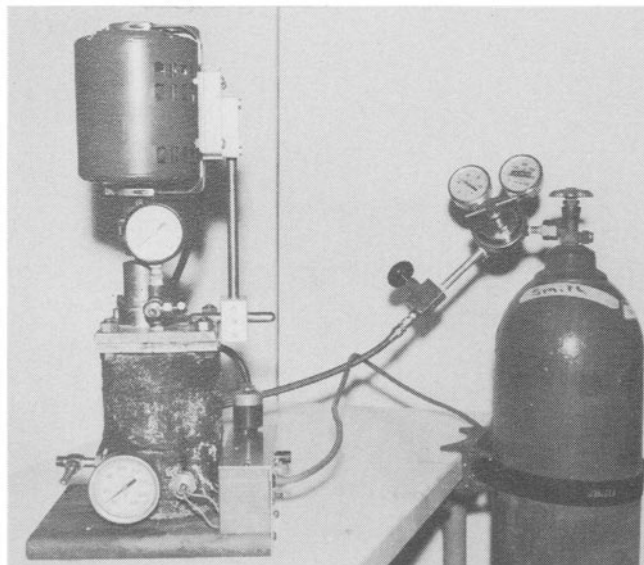


FIG. 1. Laboratory pressure reaction apparatus used to hydrogenate 0.5 kg samples of milk fat.

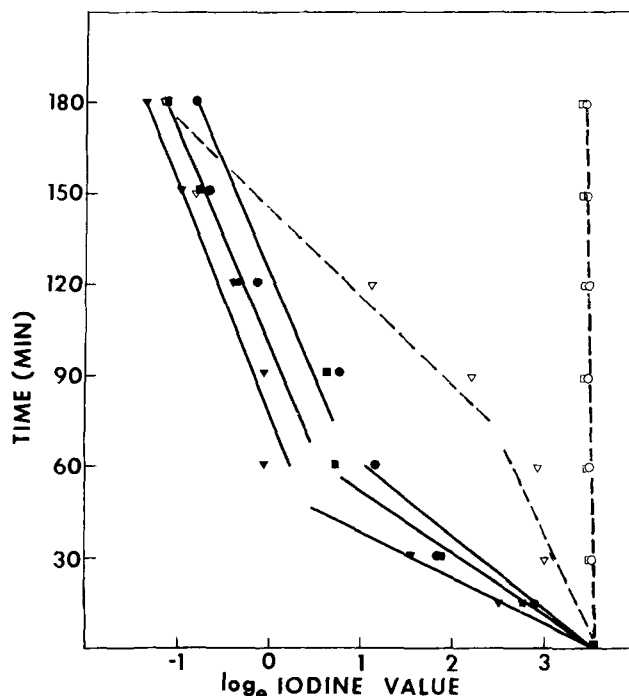


FIG. 2. Kinetic plot indicating effect of temperature upon hydrogenation rates at 53 psig with 0.05% palladium (solid points, solid lines) and 1.00% nickel catalyst (open points, dashed lines). Temperatures (C): 66, circles; 93, squares; 121, triangles. Two slopes indicate a change in reaction rate occurred.

TABLE I
Summary of Conditions Used In Hydrogenation of Milk Fat

Variable	Catalyst	Concentration percent			Pressure psig			Temperature C		
Temperature	Palladium nickel	0.050			53			66 93 121		
		1.00			53			66 93 121		
Pressure	Palladium nickel	0.050			15	30	53	121		
		1.00			15	30	53	121		
Catalyst concentration	Palladium nickel	0.005	0.025	0.050	53			121		
		0.05	0.50	1.00	53			121		

catalyst were heated to the temperature of hydrogenation. Air and traces of moisture were removed by coming up to and releasing the hydrogen pressure two or three times at the beginning of the experiment. Speed of the reactor stirrer was kept constant at 1500 rpm during the 180 min hydrogenations. Samples of ca. 10 g were taken at 15 min intervals during the first hr, and at 30 min intervals thereafter. Immediately after hydrogenation, activated charcoal was mixed with each sample to a concentration of 2%. The sample then was filtered at 60-65 C through Schleicher and Schuell filter paper 560 to remove the catalyst. Hydrogenation was followed during the process by the refractive index of the sample at 60 C.

Analytical Methods

American Oil Chemists' Society methods Cc7-25, Cc2-38, Cd7-58, and Cd14-61 (10) were used to determine refractive index, Wiley mp, and concentrations of conjugated polyunsaturated acids and isolated *trans*-isomers, respectively, of the samples. Hanus iodine values (IV) were obtained by the Association of Official Analytical Chemists' methods (11).

Methyl esters of fatty acids were prepared from the fats by the alcoholysis method of Christopherson and Glass (12). Ester mixtures were analyzed with a Varian Aero-

graph 1200 chromatograph equipped with a flame ionization detector and a 7.3 m x 2 mm inside diameter glass column packed with 70/80 chromosorb G coated with 2% DEGS. Gas flow rates for nitrogen, hydrogen, and air were 25, 30, and 750 ml/min, respectively. Injector and detector temperatures were 210 and 270 C, respectively. The column was temperature programmed from 45-196 C at a rate of 4 C/min. Chromatogram peaks were identified by comparing their retention times with those of authentic mixtures of pure methyl esters. An internal standard, C₉ methyl ester, was added to each sample to overcome the variation in sample injections.

Peak areas were integrated with an Infotronics CRS 104 digital integrator equipped with BP-100 baseline projection. The output was recorded on a T-33 standard teletype with paper tape. The paper tape then was used to generate a magnetic tape via timeshare mode to the campus Burroughs B5500 computer for a permanent record. A program was written to enter the stored data from integrated analyses and to plot simulated chromatograms using a Cal-Comp Plotter model 750 under computer control. Simulated Gaussian curves specifically were selected to match peak width and retention times of the original chromatograms. Individual chromatograms then were plotted successively behind each other to generate a three dimensional topo-

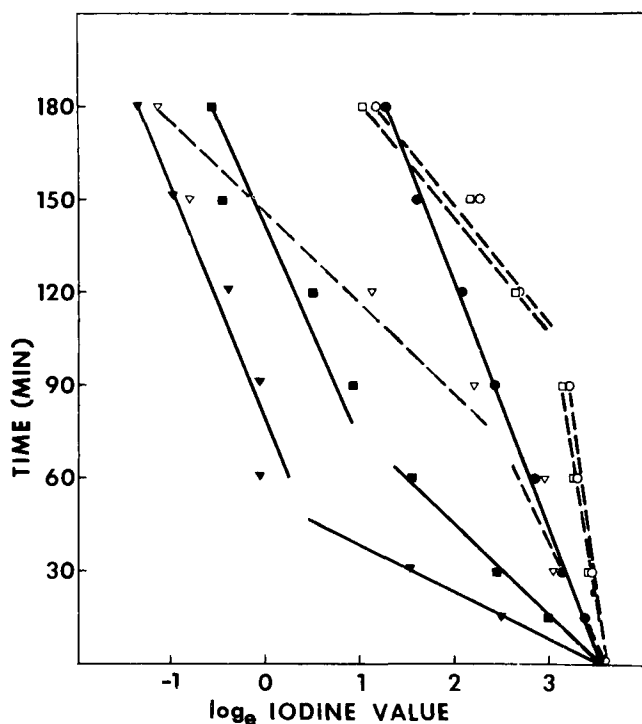


FIG. 3. Kinetic plot indicating effect of pressure upon hydrogenation rates at 121 C with 0.05% palladium (solid points, solid lines) and 1.00% nickel catalyst (open points, dashed lines). Pressures (psig): 15, circles; 30, squares; 53, triangles. Two slopes indicate a change in reaction rate occurred.

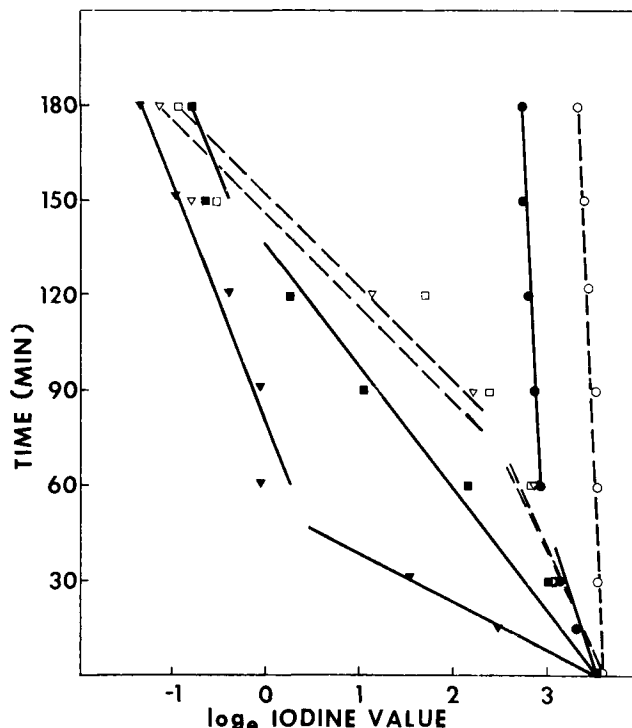


FIG. 4. Kinetic plot indicating effect of catalyst concentration upon hydrogenation rates at 53 psig and 121 C. Palladium concentrations (percent): 0.005, ●; 0.025, ■; 0.050, ▲. Nickel concentrations (percent): 0.005, ●; 0.025, ■; 0.050, ▲. Nickel indicate a change in reaction rate occurred.

TABLE II

Effect of Kind and Concentration of Catalyst Upon Iodine Values and Wiley mp of Milk Fat Hydrogenated at 121 C and 53 psig

Hydrogenation time (min)	Palladium (percent)			Nickel (percent)		
	0.005	0.025	0.050	0.05	0.50	1.00
mp						
0	32.4	34.3	32.4	32.4	32.4	32.4
30	39.9	40.1	49.3	33.8	35.5	37.4
60	40.6	45.0	49.8	34.0	37.2	38.4
90	43.0	46.5	49.9	34.8	39.7	41.9
120	43.8	48.3	49.9	37.6	43.2	46.1
150	44.2	48.9	50.1	38.0	46.2	49.3
180	44.6	49.2	50.2	38.6	46.9	49.4
IV ^a						
0	35.1	35.1	35.1	36.8	35.1	36.8
30	22.6	20.2	4.7	34.5	21.5	21.6
60	18.5	8.6	1.0	33.7	17.8	19.0
90	17.6	2.8	0.9	33.5	11.0	9.1
120	16.3	1.3	0.7	31.7	5.4	3.1
150	15.6	0.5	0.4	29.9	0.6	0.4
180	15.4	0.4	0.2	28.1	0.4	0.3

^aIV = iodine values.

logical display in which differences among the plotted chromatograms were readily discernible.

RESULTS AND DISCUSSION

The working range of hydrogenation variables was determined from preliminary experiments, and the conditions selected are summarized in Table I. Changes in refractive index provided a simple, fast, but relatively insensitive means to follow the progress of hydrogenation. Indices ranged from 1.4471 for control milk fats (IV 35.1) to 1.4433 for fully hydrogenated samples (IV < 1.0). Decreases in refractive index paralleled decreases in IV and increases in mp.

Effect of Temperature and Pressure

With palladium as catalyst, the decreases in IV and the increases in mp followed similar trends at 66, 93, and 121 C. The hydrogenation rate was rapid at each temperature but was slightly greater at 121 C. In 30 min, at this temperature, the IV was decreased from 35.1 to 4.7, and the mp was increased from 32.4-49.3 C. In the kinetic plot of the reaction (Fig. 2), the two slopes for each temperature indicate a change in reaction rate occurred at each temperature. The initial rates were faster up to 60 min.

Temperature had a marked influence on hydrogenation

when the catalyst was nickel. Complete hydrogenation was only achieved at 121 C, and 120 min were required at this temperature to reduce the IV to 3.1 and increase the mp to 46.1 C. The kinetic plot (Fig. 2) indicates that the rate of reaction at 121 C was faster after 60 min.

With palladium as catalyst, the higher the pressure, the greater was the rate of reaction. At 15 psig, the rate decreased fairly uniformly; but at 30 and 53 psig, the initial rapid rates slowed markedly as the IV approached 4.0. There were corresponding trends when mp were plotted against times of reaction. The kinetic plot (Fig. 3) for 15 psig follows first order kinetics and has a single slope. There was a progressive change to two sloped curves at 30 and 53 psig. At both pressures, the initial rates up to 60 min were faster.

The decreases in IV at each pressure were more gradual with nickel as catalyst than with palladium. Increasing the pressure from 15 to 30 psig did not affect the rates of changes in IV or mp. The changes were accelerated at 53 psig, and at 180 min the milk fat was almost completely saturated. The kinetic plot (Fig. 3) has two sloped curves for each pressure, indicating that the rates of reaction increased during the latter stages of hydrogenation.

Effect of Kind and Concentration of Catalyst

The kind and concentration of catalyst had a marked

TABLE III

Changes in Total Unsaturated, Conjugated, and *Trans*-Acids of Milk Fat During Hydrogenation with Palladium or Nickel Catalyst

Catalyst	IV ^a	Total unsaturated acids percent	Conjugated acids percent			<i>Trans</i> -isomers ^b percent
			diene	triene	tetraene	
Control	35.1	35.2	1.10	0.024	0.004	29
Palladium (0.050%)	25.7	31.1	0	0	0	34
	20.2	26.9	0	0	0	56
	8.6	12.7				27
	4.7	3.3				7
	0.3	<2				0
Nickel (1.00%)	28.4	31.5	0	0.002	0	8
	21.5	24.6	0	0	0	10
	9.1	14.1				15
	3.1	---				17
	0.3	<2				0

^aIV = iodine values.^bExpressed as percent of total unsaturated fatty acids.

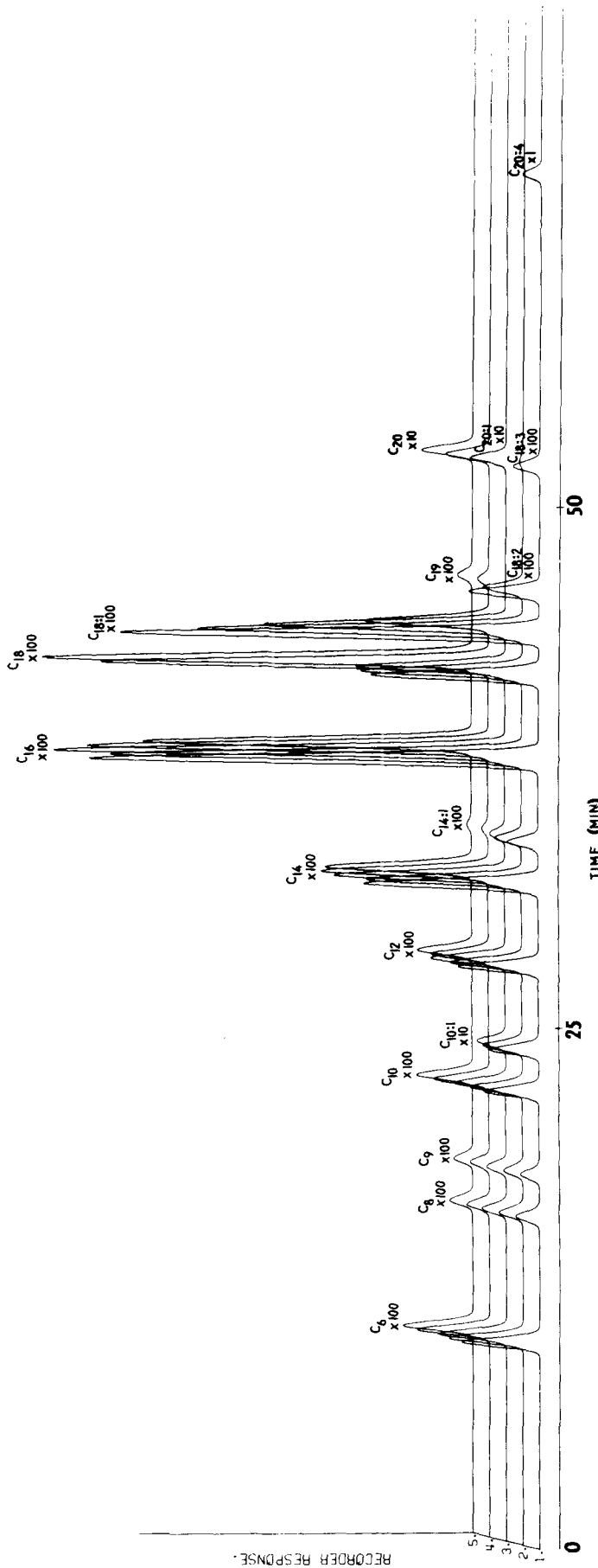


FIG. 5. Computer generated, three dimensional profile representing important peaks selected from five sequential gas liquid chromatograms of milk fat hydrogenated with nickel catalyst. Individual chromatograms 1-5 are plotted successively behind each other in order of decreasing IV -36.8, 27.0, 21.5, 3.1, and 0.3. Peak C₉ is the internal standard. The progressive decreases in the unsaturated peaks are matched by increases in the corresponding saturated peaks. Note that C_{20:4}, C_{18:3}, and C_{18:2} disappear earlier than C_{18:1}, C_{14:1}, and C_{10:1}.

effect upon the reaction (Table II). The lowest concentration of palladium (0.005%) did not result in complete hydrogenation, and the highest mp reached was 44.6 C. With 0.025% and 0.050% palladium, hydrogenation was essentially complete. The kinetic plot (Fig. 4) indicates an increase in reaction rate after 60 min for the highest concentration.

The lowest concentration of nickel (0.05%) also did not result in complete hydrogenation (Table II). At the two higher concentrations (0.50% and 1.00%), hydrogenation was complete; and the rates of hydrogenation were similar, as were changes in IV and mp. The kinetic plot (Fig. 4) indicates two reaction rates with the slower at the beginning of the process.

Although the concentration of nickel catalyst was 20 times greater, reduction in IV was much slower with nickel than with palladium at 121 C and 53 psig. The kinetic plot (Fig. 4) reveals two rates of reaction for both catalyst, with a breakpoint around 60 min. The palladium curve indicates a fast rate followed by a slower rate, whereas nickel produced a slow rate at first and then a faster rate. The reaction rate constants k_1 and k_2 for palladium were 1.10×10^{-3} and $2.20 \times 10^{-4} \text{ sec}^{-1}$, respectively. For nickel, k_1 and k_2 were 2.56×10^{-4} and $5.73 \times 10^{-4} \text{ sec}^{-1}$, respectively. The double kinetic slopes indicate that during the later stages of hydrogenation, palladium was inactivated partially, but nickel was activated further. The data for nickel confirm the report of Yoncoskie, et al., (6) who found two distinct slopes for hydrogenation of milk fat with 1% Raney nickel catalyst at 120 C and 15 psig.

Changes in the more important fatty acids during hydrogenation with nickel catalyst are indicated in Figure 5. As hydrogenation proceeded, there were progressive decreases in the unsaturated series of acid and compensating increases in the corresponding saturated acids. Polyunsaturated peaks disappeared earlier than did monounsaturated. Appreciable amounts of saturated C_{19} and C_{20} acids were formed as the corresponding unsaturated acids were hydrogenated. A similar pattern of changes was obtained with palladium catalyst, except that the polyunsaturated acids were hydrogenated more rapidly. At an IV of 25, linoleic and linolenic acids were transformed completely to monounsaturated acids without increasing the stearic acid content.

Table III contains a further comparison between milk fat hydrogenated with palladium and that hydrogenated with nickel. For the same units of IV lowered, the decreases in total unsaturated acids, as determined by gas liquid chromatography, agreed. With both catalysts, conjugated fatty acids disappeared at the beginning of hydrogenation. It is probable that any intermediate conjugated polyunsaturated acids would be hydrogenated rapidly, and occur at levels too low to detect. With palladium, there was a marked increase in the relative percentages of *trans*-isomers present until the IV was reduced below 10. This result is consistent with the well known tendency of palladium catalyst to produce *trans*-isomers (13).

With both catalysts, the original color of milk fat was bleached during the early stages of hydrogenation. Also, an off-flavor, which was more pronounced with nickel cata-

lyst, developed during the process. The possibility of removing this off-flavor by treatments, such as washing with water or deodorization, should be investigated.

The choice of catalyst and other parameters for hydrogenation of milk fat depends upon several factors, including planned use of the hydrogenated fat, equipment available, and costs. Commercial anhydrous milk fat is not refined and includes a complex mixture of triglycerides, diglycerides, monoglycerides, free fatty acids, free sterols, sterol esters, and carotenoids (14). Refining might remove catalyst poisons and permit the use of lower concentrations of catalyst but would increase the cost of the anhydrous milk fat. Both palladium and nickel catalysts could be removed readily by filtration after the reaction. Vasishtha, et al., (5) have recommended a palladium catalyst for selective trace hydrogenation of milk fat. The present study confirms that palladium is a much more active catalyst than nickel. Complete hydrogenation was achieved rapidly with palladium at 66 C, compared to a slower rate with nickel at 121 C. This slower rate might facilitate control of the process to obtain partially hydrogenated milk fat fractions of specific IV and mp, but the use of smaller amounts of palladium catalyst also would slow the reaction. The questions of selectivity and formation of *trans*-isomers are less critical with milk fat than with most vegetable oils because of its much lower original polyunsaturated fatty acid content and low final IV.

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