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❖ Heterogeneous Catalytic Hydrogenation of Canola Oil Using Palladium

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The hydrogenation of canola oil was studied using palladium black as a potential catalyst for producing partially hydrogenated fats with low *trans*-isomer content. Pressure (150-750 psig) appeared to have the largest effect on *trans*-isomer formation. At 750 psig, 90 C and 560 ppm metal concentration, a maximum of 18.7% *trans* isomers was obtained at IV 53. A nickel catalyst produces about 50% *trans* isomers at the same IV. For palladium black, the linolenate and linoleate selectivities were 1.2 and 2.7, respectively. The maximum level of *trans* isomers observed ranged from 18.7% to 42.8% (150 psig). Temperature (30-90 C) and catalyst concentration (80-560 ppm) affected the reaction rate with little effect on *trans*-isomer formation and selectivities. At 250 psig and 50 C, supported palladium (5% Pd/C) appeared to be twice as active as palladium black. At 560 ppm Pd, 5% Pd/C produced 30.2% *trans* (IV 67.5), versus 19.0% *trans* for palladium black (IV 68.9). Respective linoleate selectivities were 15 and 6.6, while linolenate selectivities were approximately unity. Analysis of the oil samples by neutron activation showed approximately a 1 ppm, Pd residue after filtration.

The search is still on for an active, heterogeneous catalyst for hydrogenation of edible oils with production of a low level of *trans* isomers. The need for such a catalyst arose following a Canadian study which reviewed the health effects of these isomers (1). This subject was reviewed thoroughly by Applewhite (2). In his review it was shown that the studies of the health effects of *trans* isomers were inconclusive. The FDA recently commissioned the Federation of American Societies for Experimental Biology to undertake a study of *trans* fatty acids (3) in the hope of settling this controversial issue. Thus, we feel it would be prudent to develop alternative catalysts which would minimize the formation of *trans* fatty acids. Such a development would, in any case, offer the processor an alternative, should one be needed, for this or any other reason.

In an earlier review of catalysts (4), it was reported that heterogeneous palladium catalysts were unsuitable for the hydrogenation of triglycerides because they were nonselective and produced large quantities of *trans*

acids. More recent work indicates that, in general, palladium forms more *trans* isomers than nickel (5), especially under conditions normally employed with the latter (6). Thus, we initially investigated the homogeneous catalytic hydrogenation of canola oil using a palladium complex. It had been reported by Itatani and Bailar (7) that the mixture of dichlorobis(triphenylphosphine) palladium (II) and stannous (II) chloride dihydrate was a very active homogeneous catalyst for the hydrogenation of soybean oil methyl esters. Furthermore, at 575 psi and 60 C, a total *trans* content of less than 20% was observed. We used this catalyst mixture to hydrogenate canola oil at 500 psig and 110 C. After 5 hr of reaction time the IV dropped 12 units. A black precipitate, most likely palladium, was present in the partially hydrogenated oil. Itatani and Bailar (7) reported that some of their runs produced a precipitate. In another report (8), the same authors observed a black precipitate following the hydrogenation of soybean oil methyl ester using the platinum analog of the palladium complex. The precipitate, assumed to be platinum black, was then used in a run, but it proved to be relatively inactive. We observed that our precipitate, when used alone in the hydrogenation of canola oil, was very active at 750 psig and 70 C. The homogeneous palladium catalyst subsequently was abandoned, and palladium black was made the catalyst of choice. The objective of our study was, therefore, to evaluate the performance of palladium with respect to pressure, temperature, concentration and catalyst support during the hydrogenation of canola oil.

The earliest published work on the hydrogenation of any edible oil in which palladium was used was in 1953; in it, the promoter effect of platinum and palladium on nickel was examined (9). It was found that the addition of platinum increased the bonding strength of hydrogen to the catalyst surface, whereas addition of palladium decreased the bonding strength. Zajcew (10) hydrogenated castor oil to castor wax using 5% and 1% palladium on carbon. Although palladium on carbon was used by Zajcew in subsequent reports (11,12), it was for the hydrogenation of soybean and cottonseed oil. In almost all cases, hydrogenation was accompanied by 20-50% *trans*-isomer formation. The lowest *trans* content reported was 15.0% at IV 67.1 (11). The catalyst used was palladium (200 ppm) in the form of 1%

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palladium on carbon, partially deactivated by silver and bismuth. The author also claimed that this modified palladium catalyst showed improved selectivity over supported palladium alone. Riesz and Weber (5) observed that the use of barium sulphate as a carrier for palladium suppressed *trans*-isomer formation without appreciably affecting activity or selectivity. The authors evaluated the selectivity and *trans*-isomer formation of platinum, palladium and rhodium on various supports. In general, these catalysts showed a higher selectivity and *trans* content than either supported or unsupported nickel catalysts in the hydrogenation of soybean oil.

Russian workers studied the hydrogenation of cottonseed oil using palladium catalysts (13-19). Cottonseed oil was selectively hydrogenated in solvents such as ethanol, methanol, butane and propane using palladium with platinum, nickel, cobalt and copper as additives (13). Addition of 0.01% platinum to an oil hydrogenated in the presence of 1% palladium by weight resulted in a lowering of the *trans* content from 37.4% to 17%. Kozina et al. (14) investigated cottonseed oil hydrogenation in solvents using the mixed noble metals palladium-platinum (3:1) and palladium-ruthenium (9:1). Platinum, palladium and ruthenium also were used individually. The catalysts were supported on silica gel, carbon and alumina. In order of decreasing activity, the catalysts were palladium-ruthenium, palladium, palladium-platinum and platinum. The minimum *trans* content obtained was 25% using 3:1 palladium-platinum on alumina. Palladium on alumina gave 37.3% *trans*. It was further observed that after 40 hr of continuous processing palladium, palladium-ruthenium and palladium-platinum did not lose their activity, in comparison with Raney nickel, which showed a decrease in activity after eight hr. Further work on mixed palladium-platinum catalysts was done by Sokol'skii et al. (20). Ahmad et al. hydrogenated soybean oil using 1-10% palladium supported on carbon at hydrogen pressures between ambient and 70 psig and at temperatures between 80 C and 160 C in three types of stirred reactors (6). It was concluded in that study that if palladium is deposited on the exterior of the carbon so that it is accessible to triglyceride molecules, its selectivity and activity were superior to those of nickel, even at temperatures at which nickel is inactive. It also was found that palladium catalysts produced more *trans* isomers than nickel at higher temperatures.

To date only one publication has been found on the use of palladium as a catalyst in the hydrogenation of low erucic acid rapeseed (LEAR) oil (21). Carbon-supported palladium was used at room temperature. It was found that the IV of LEAR oil dropped from 109.7 to 83.8 in 40 min at 70 psig, using 0.1% (1000 ppm) of palladium. A *trans*-isomer content of 14.7% was reported. For the hydrogenation, linolenate and linoleate selectivities were 2.5 and 14.7, respectively.

The most recent publication on supported palladium dealt with the use of the catalyst for hydrogenation of soybean oil (22). Commercially available 5% palladium-on-carbon was used to determine its behavior during hydrogenation. Empirical models were developed which predicted the rate, *trans*-isomer formation and selectivity over a range of practical reaction conditions. It was found that palladium offered no special advantage in

either *trans*-isomer formation or selectivity over nickel catalysts.

EXPERIMENTAL

Materials and methods. Refined, bleached and deodorized canola oil was supplied by Canada Packers Ltd., Toronto. The oil was rebleached using 0.5% w/w of bleaching clay (Vega Plus) under a nitrogen atmosphere with continuous agitation at room temperature for one hr. Palladium black and 5% palladium-on-carbon were purchased from Strem Chemicals Inc., Newburyport, Massachusetts.

Hydrogenations were carried out in a 300-ml Parr Pressure Reactor (Parr Instrument Co., Moline, Illinois) at an agitation rate of 830 rpm. A charge of 100 g oil was used for each run. The catalyst plus oil were heated in the reactor while under nitrogen. The zero time of the reaction corresponded to the introduction of hydrogen into the reactor.

The reaction was monitored by measuring the refractive index of the hydrogenated oil samples removed periodically during the run. The approximate IV of the filtered oil was calculated from a pre-calibrated curve of refractive index vs IV. The IV's used in this report were calculated from GLC data. The rate of IV reduction was assumed to be first-order with respect to IV.

Analyses were done according to standard AOCS methods. The *trans*-isomer content was determined using a Nicolet 60 SX FTIR spectrophotometer. Separation of the methyl esters was achieved by GLC using a 30 m SP-2330 coated glass capillary column (Supelco Inc., Bellefonte, Pennsylvania). The metal content in the oil was determined by neutron activation analysis using the SLOWPOKE Reactor of the University of Toronto.

RESULTS AND DISCUSSION

Effect of pressure. The effect of pressure was studied at 50 C and 90 C using a catalyst loading of 56 mg/100 g oil, or 560 ppm, of palladium. From the results at 90 C (Fig. 1A, Table 1), it can be seen that a 5 fold increase in pressure from 150-750 psig increased the overall rate constant by 29%, from 5.06×10^{-2} to $6.51 \times 10^{-2} \text{ min}^{-1}$. At 50 C, however, (Table 1), an increase in pressure from 250 to 750 psig resulted in a 130% increase in the rate constant, from 1.75×10^{-2} to $4.02 \times 10^{-2} \text{ min}^{-1}$. It is most likely that at 90 C the reaction is approaching the region of pore mass-transfer limitation. The *trans* content exhibited decreasing maxima with increasing pressure (Fig. 1B). For the runs at 150, 250 and 750 psig, the respective maximum *trans* values were 42.8%, 35.4% and 18.7%. Specific isomerization index, SII, defined as $[\% \text{ trans}/(\text{IV}_t - \text{IV}_0)] \times 100$ is given for each run (Table 1). As seen from the table, increasing the pressure from 250 to 750 psig results in the SII value dropping from 82 to 34.6, a decrease of 58%. A similar decrease in SII, from 53.0 to 25.9, is observed at 50 C, for the same pressure increment. Linolenate selectivities were approximately constant over the pressure range studied, while linoleate selectivities showed an increase with decreasing pressure. At 90 C, the selectivities for 750, 250 and 150

TABLE 1
Hydrogenation of Canola Oil Using Palladium

Run ^a	Press. (psig)	Temp. (C)	Conc. (ppm)	IV ^b	Sampling Time (min)	% trans	SII	S _{Ln}	S _{Lo}	k × 100 ^c (min ⁻¹)
<i>Effect of Pressure</i>										
1	750	90	560	53.8	10	18.7	34.6	1.2	2.7	6.51
2	250	90	560	67.0	10	35.4	82.0	1.2	11.2	6.13
3	150	90	560	61.0	15	42.8	88.1	0.9	16.5	5.06
4	750	50	560	51.4	20	14.1	25.9	1.2	3.2	4.02
5	250	50	560	68.9	30	19.0	53.0	1.1	6.6	1.75
<i>Effect of Temperature</i>										
6	750	90	560	53.8	10	18.7	34.6	1.2	2.7	6.51
7	750	70	560	49.3	13	15.4	26.7	1.1	2.6	5.93
8	750	50	560	51.4	20	14.1	25.9	1.2	3.2	4.02
9	750	30	560	92.0	150	6.6	30.9	1.6	4.4	0.13
10	750	90	150	58.6	35	15.8	31.3	1.2	2.9	1.87
11	750	70	150	59.4	50	17.0	32.9	1.1	3.2	1.28
12	750	50	150	86.7	50	7.5	26.8	1.1	2.9	0.51
13	750	90	61	68.2	300	21.1	43.8	1.3	3.1	0.18
14	750	70	64	67.6	300	15.0	32.0	1.2	2.5	0.18
15	750	60	71	73.2	360	13.5	31.6	1.1	2.5	0.13
16	750	50	80	98.1	360	6.6	34.4	1.1	3.1	0.05
<i>Effect of Catalyst Concentration</i>										
17	750	50	560	51.4	20	14.1	25.9	1.2	3.2	4.02
18	750	50	276	85.8	20	6.4	23.3	1.1	2.8	1.34
19	750	50	148	86.7	50	7.5	26.8	1.1	2.9	0.51
20	750	50	80	98.1	360	6.6	34.4	1.1	3.1	0.05
<i>Effect of Catalyst Support</i>										
21	250	50	560	68.9	30	19.0	53.0	1.1	6.6	1.75
22 ^d	250	50	560	67.5	20	30.2	60.7	1.4	15.0	3.90

^aRun # does not correspond to actual runs done as some are repeated in the table.

^bIV of sample with the highest trans. Starting IV is 115.

^cCalculated assuming first order reaction rate with respect to IV.

^dRun using 5% palladium on carbon.

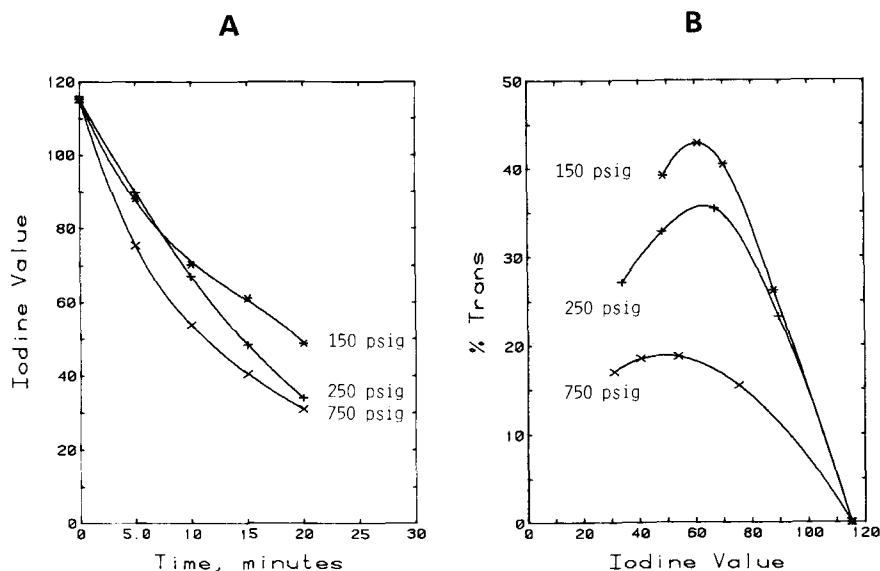


FIG. 1. Effect of pressure at 90 C, 560 ppm Pd.

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psig are respectively 2.7, 11.2 and 16.5.

It has been demonstrated conclusively (23,24) that polyunsaturated fatty acids, rather than monoenoic acids, are preferentially adsorbed onto a nickel catalyst surface. It is reasonable to assume that the same would hold true for the palladium catalyst. Thus, it would be expected that the linoleate selectivity would decrease with an increase in pressure (25). At a higher pressure, due to a higher surface concentration of hydrogen, a significant proportion of the polyunsaturated fatty acid may never reach the polybonded state on the catalyst surface. The initial state (26) therefore will be the same for both polyunsaturated and monounsaturated fatty acids, and there would be an equal chance of reaction for both adsorbed species via the half hydrogenated state. This is further illustrated (Fig. 2) by the rapid decrease in the monoene content at 750 psig with a corresponding rise in saturate content, unlike at 250 psig where the trienes and dienes monopolize the surface and react first.

Effect of temperature and catalyst concentration. The temperature effect on canola hydrogenation was studied

at three catalyst concentrations: 560 ppm, 150 ppm and 60-80 ppm palladium. The pressure used was 750 psig. It was observed that using 560 ppm palladium at 30 C resulted in hydrogenation of the oil. The rate constant was $0.13 \times 10^{-2} \text{ min}^{-1}$ (Table 1). At 50 C the rate constant was $4.02 \times 10^{-2} \text{ min}^{-1}$, a 30 fold increase over the 20 C temperature increment (Fig. 3). Subsequent 20 C temperature increments produced rate constants of 5.93 and $6.51 \times 10^{-2} \text{ min}^{-1}$ at 70 C and 90 C, respectively.

It is plausible that at 30 C the hydrogenation is kinetically controlled, and smaller temperature increments will result in gradual rate increases. At 70 C and higher the reaction would be limited by the diffusion of the triglyceride molecules to the catalyst surface, as reflected by the relatively smaller increase in the rate constant from 70-90 C over the catalyst concentration range (Table 1). Mass transfer from the hydrogen bubbles to the oil is not the controlling factor, as a zero order reaction would prevail (27). A pseudo-first order reaction with respect to IV was observed for all the runs.

For a given IV, the *trans* content increases with

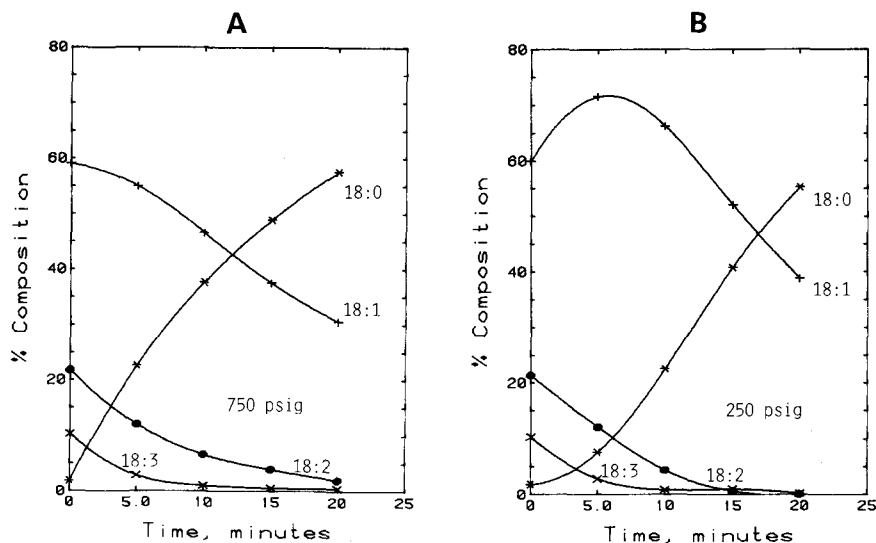


FIG. 2. Effect of pressure on composition at 90 C, 560 ppm Pd.

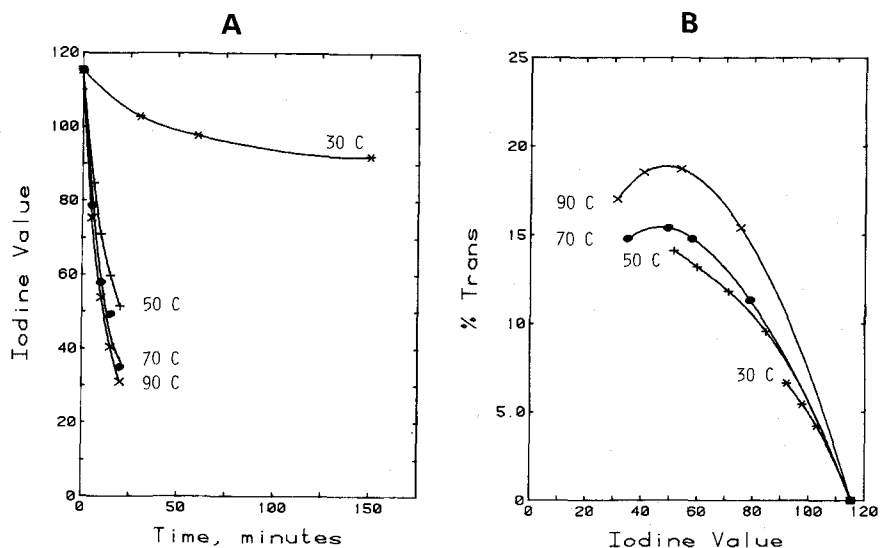


FIG. 3. Effect of temperature at 750 psig, 560 Pd.

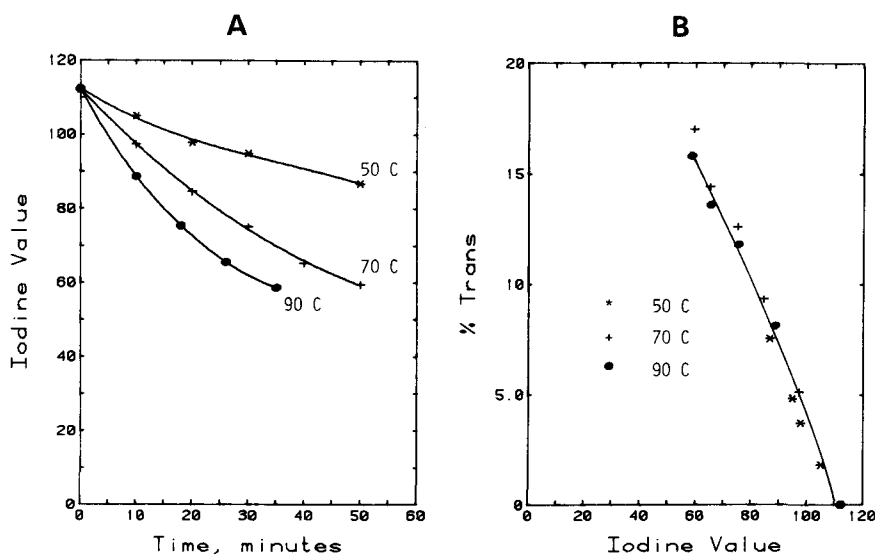


FIG. 4. Effect of temperature at 750 psig, 150 ppmPd.

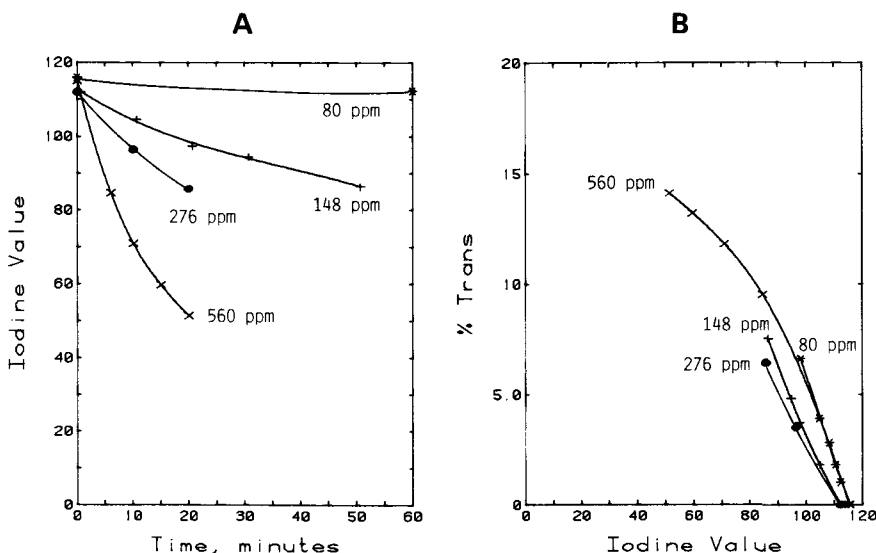


FIG. 5. Effect of catalyst concentration at 750 psig, 50 C.

increasing temperature (Fig. 3B). SII values indicate that approximately 25-35% of the bonds hydrogenated result in *trans*-isomer formation in the 30-90 C range. These values compare favorably with those calculated for the homogeneous catalytic hydrogenation of canola using $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ (28). A 20 C increase in temperature resulted in a 25% decrease in linolenate selectivity, from 1.6 to 1.2 (Table 1), with no change thereafter for 20 C increments through to 90 C. Linolenate selectivity levelled off at 2.6 (70 C) from 4.4 (30 C).

A catalyst level of 150 ppm resulted in a lower hydrogenation rate, as expected, when compared at the same temperature and pressure conditions (Table 1). At 50 C, for example, a decrease in catalyst concentration from 560 ppm to 150 ppm resulted in an 87% decrease in the rate constant, from 4.02×10^{-2} to $0.51 \times 10^{-2} \text{ min}^{-1}$. The total *trans* content (Fig. 4B) and linolenate and linolenate selectivities (Table 1), however, showed

almost no variation over the 40 C range. Interpolation of the curves at 50 and 70 C (Fig. 4A) would result in a run at 60 C with a hydrogenation rate of approximately one IV drop per min. This rate is typical of that used in the industry. Thus, a practical hydrogenation rate can be realized using palladium black at a level of only about 6% of commercial nickel catalyst, commonly used in industry. Furthermore, less than 20% of *trans* isomer is formed, compared with about 50% using a nickel catalyst.

At 50 C and a catalyst concentration of 60-80 ppm, the rate constant was $0.05 \times 10^{-2} \text{ min}^{-1}$ compared with $0.51 \times 10^{-2} \text{ min}^{-1}$ at the same temperature for the catalyst loading of 150 ppm (Table 1). It should be noted that the order of magnitude decrease in the rate constant also was observed at 90 C for the given catalyst levels. The *trans* content for 60-80 ppm palladium was insensitive to the temperature rise from 50-70 C;

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however, at 90 C a trend toward higher *trans* was observed (Table 1). Selectivities remained constant.

Catalyst concentrations of 80 to 560 ppm were studied at 50 C and 750 psig. The high pressure and low temperature were selected to minimize *trans*-isomer formation. It was observed that only the rate was significantly affected by changes in the catalyst concentration (Fig. 5A), while *trans*-isomer content (Fig. 5B) and selectivities were relatively unaffected (Table 1).

Trans-isomer formation and selectivities were relatively insensitive to temperature and catalyst concentration when compared to pressure. It is expected that both the *trans*-isomer content and selectivity would increase with temperature and catalyst concentration, due to the increasing demand of the dissolved hydrogen concentration near the catalyst surface (25). This was observed at 250 psig (runs 2 and 5 of Table 1). At 750 psig, however, it is plausible that the dissolved hydrogen supply near the catalyst surface is high enough that the increase in temperature and catalyst concentration would not affect isomerization and selectivity. Furthermore, in a study by Coenen et al. (29) it was reported that the selectivity was poorer with supported nickel catalysts having an average pore diameter of 27 Å than with those of average diameters of 34 and 66 Å. The diameter of the triglyceride molecule, calculated as a sphere, was estimated to be 15 Å, indicating a highly restricted rate of diffusion within the pores of diameter 27 Å. It is likely that in the case of palladium, too, selectivity is strongly dependent on pore size. Increase in temperature and catalyst concentration then would not have as great an effect on selectivity as would an increase in the average pore diameter.

Comparison of supported and unsupported palladium. Reactivity of palladium (5%) on carbon was compared to palladium black. Experimental conditions were 250 psig, 50 C, and 560 ppm metal concentration. The results clearly showed that the supported palladium is more active (Fig. 6A). The IV dropped to 35 in 30 min,

compared to 69 in the same time for palladium black. Respective rate constants were 3.9×10^{-2} and $1.75 \times 10^{-2} \text{ min}^{-1}$. *Trans*-isomer formation also was enhanced in the case of Pd/C (Fig. 6B). At IV 70 Pd/C produced 30% *trans*, compared with 20% for palladium black. Linoleate selectivities were higher for Pd/C than for palladium (Table 1). Linolenate selectivities were 1.36 and 1.09 for Pd/C and palladium, respectively. A linoleate selectivity of 14.7 was obtained by Cecchi et al. (21), using 1000 ppm palladium (5% Pd/C) in LEAR oil at 70 psig, 20-25 C. A direct comparison cannot be made to the work of Cecchi et al. as the reaction conditions used were very different from those used by us.

It is likely that the observed increase in activity is due to the higher effective metal concentration in the case of supported palladium. The sponge-like structure of palladium black (Fig. 7A) suggests a more tortuous diffusion path for the triglyceride molecule to gain access to the metal sites, unlike the Pd/C (Fig. 7B). Furthermore, agglomeration of the metal particles in palladium black would block the active sites within the pore. However, no conclusion can be made without further examination of the physical characteristics of the catalysts.

Residual metal in filtered oil samples. Ten hydrogenated oil samples were analyzed for residual metal using neutron activation. The samples were first filtered through a membrane filter of 0.45 μm pore size. It was found that the palladium concentration obtained after filtration was 0.8 (± 0.2) ppm. This residual metal is most likely due to metal particles smaller than 0.45 μm as, unlike nickel, palladium forms no soaps (30). This result supports the conclusion that the catalytic hydrogenation is indeed heterogeneous.

In summary, our work strongly suggests that palladium black is a potential catalyst for the hydrogenation of canola oil. Its activity at low temperature (30-90 C) and its ability to give low *trans*-isomer content are distinct advantages over

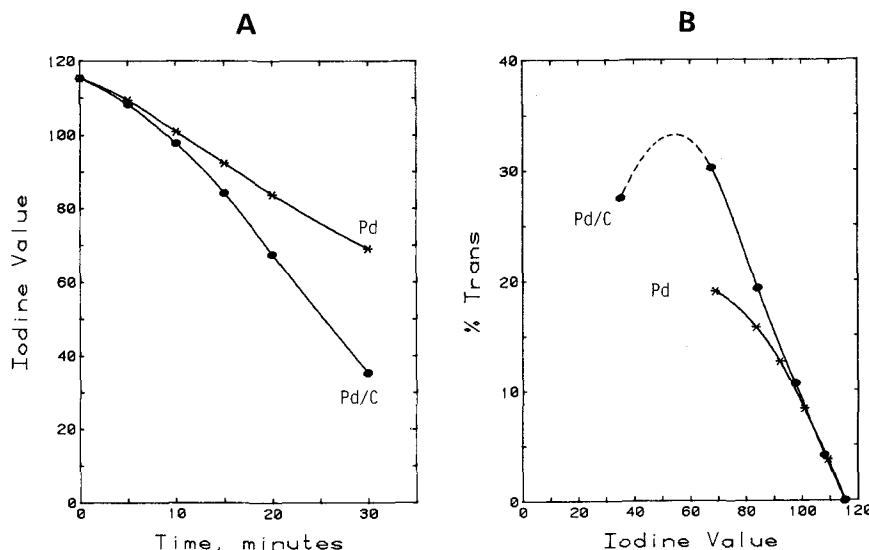


FIG. 6. Comparison of supported and unsupported Pd, 560 ppm, at 250 psig, 50 C.

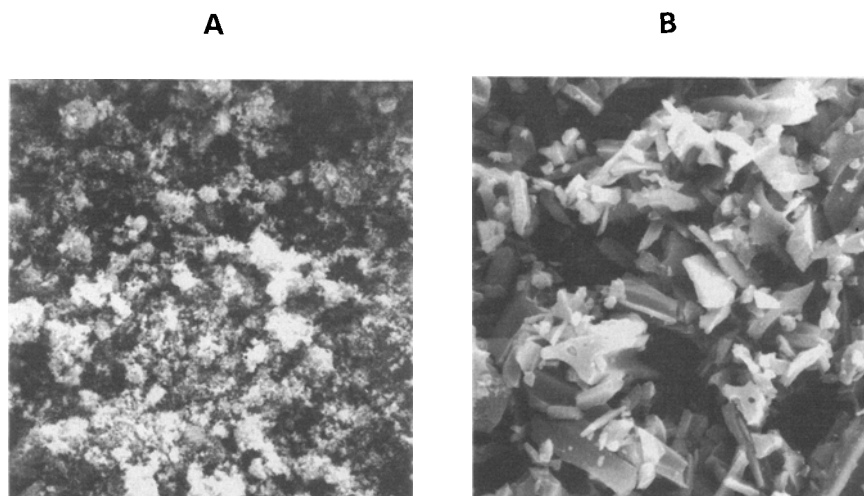


FIG. 7. Micrographs of palladium. A, palladium black (1000x); B, 5% palladium on carbon (1000x).

presently used nickel catalysts. Palladium is used at 50-150 times lower concentration than nickel. Hence, recycling this catalyst three times will be sufficient to make it price competitive with nickel. At present palladium is 150-250 times more expensive than nickel. The reusability of palladium black directly, or on an inert support to facilitate its recovery, is under investigation. Work also is continuing on the detailed investigation of the reaction mechanism of the catalysts.

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