Catalytic Transfer Hydrogenation of Soybean Oil

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The catalytic transfer hydrogenation of soybean oil by various hydrogen donors and solvents with palladium-on-carbon catalyst was investigated in batch and continuous modes. The choice of reaction conditions, donor and catalyst allowed the manufacture of partially hydrogenated oils or semi-solid fats with controlled fatty acid contents, iodine value, melting point and solid content index. The level of "iso" forms of fatty acids was similar to, and average initial selectivity was higher than that obtained with gaseous hydrogenation under pressure with a catalyst of the same type. The best results were obtained in aqueous solution with sodium formate as hydrogen donor at 60°C.

KEY WORDS: **Batch hydrogenation, catalytic transfer hydrogenation, continuous hydrogenation, sodium formate, soybean oil.**

The basic hydrogenation process of edible oils means conversion of liquid oils into semi-solid substances with desired melting characteristics and partially hydrogenated oils of increased stability. Plastic vegetable fats are useful for preparing margarine and special-purpose fats, and partially hydrogenated oils are useful for high-temperature baking oils. Physical properties of a fat, especially melting point (MP) and solid content index (SCI), depend on the position of fatty acids in the triglyceride molecule as well as on their degree of unsaturation. During the hydrogenation process, highly unsaturated fatty acids are progressively converted to the saturated state, *i.e.*, linolenic (Le) to linoleic (L), then to oleic (O), and finally to stearic acid. Hydrogenation is further complicated by simultaneous double bond isomerization, which may be positional or geometrical. Since palladium-on-carbon catalyst is widely used in catalytic transfer hydrogenation (CTH), in which organic or inorganic hydrogen donors are used rather than molecular hydrogen (1,2), we have considered this process for controlling selectivities and isomerizations. Numerous authors have emphasized that palladium on various supports may be a viable industrial catalyst with gaseous hydrogenation (GH), by working successfully even at low temperatures (below 90°C) and low pressures, and yielding reasonable isomer contents (1,3,4). This is a major advantage over the use of nickel catalysts, which yield comparable isomer contents at low temperatures but require high pressure and relatively large amounts of catalyst, which greatly adds to the cost of the operation (5). The use of palladium has been reviewed (6) and indicates no special advantage in formation of *trans*-isomers or in selectivity. Nevertheless, it could substitute for nickel at greatly reduced temperatures and catalyst concentrations. The price of palladium is a concern, but the possibility of recycling this catalyst makes it competitive with nickel (5,7,8). Zajcew (9) has succeeded in repeatedly applying the very same palladium catalyst to gaseous hydrogenation of fatty oils in a pilot-plant reactor.

Catalytic transfer hydrogenation of fats containing conjugated fatty acids, and with primary alcohols, has been investigated by several workers for nickel catalyst (10). Basu and Chakrabarty (11) have shown that secondary alcohols are even better donors and that they have a great effect on selectivity as well. Formic acid (especially their salts) were reported to be efficient hydrogen donors in the presence of palladium catalyst (12). Availability and ease of handling made these hydrogen donors superior over some other sources of hydrogen already used in CTH. Due to the insolubility in common organic solvents, some of the formates require the presence of more polar solvents, *e.g.*, acetone, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or water.

Arkad *et al.* (13) have studied CTH of fatty acid methyl esters prepared from soybean oil in a concentrated aqueous alkali formate solution and reported either selective reaction or complete saturation. When transfer hydrogenation at an acceptor (A) is performed in an aqueous emulsion, water is involved in the reaction according to the equation:

$$\begin{array}{lcl} \mathrm{HCOO^- + H_2O + Pd} & \rightarrow & \mathrm{H\text{-}Pd\text{-}H + HCO_3^-} \\ \mathrm{H\text{-}Pd\text{-}H + A} & \rightarrow & \mathrm{AH_2 + Pd} \\ \hline \mathrm{HCOO^- + H_2O + A} & \rightarrow & \mathrm{AH_2 + HCO_3^-} \end{array}$$

The most recent study disclosed this reaction as a true hydrogen transfer process actually involving two donors (water and formate) with optimal concentrations (11M) for the formate salt (14).

In this paper we introduce the use of CTH for the hydrogenation of vegetable oils and fats with successful application of formic acid salts as hydrogen donors.

EXPERIMENTAL PROCEDURES

Materials. Hydrogenations were carried out with commercial refined soybean oil, supplied from the oil factory Helios-Domžale (Domžale, Slovenia). Hydrogen donors tested were formic acid, triethylamine and sodium formate (all supplied by Merck, Darmstadt, Germany), and 10% Pd-on-carbon (Fluka, Buchs, Switzerland) was used as catalyst. All chemicals were of the highest purity available.

Batch hydrogenations. In batch processes, the oil and the hydrogen donor were dissolved in an organic solvent or mixed with water. The processes were monitored by determining fatty acids (FA) of the hydrogenated oil samples which were removed periodically during the run) by gas chromatography (GC). The IV values were calculated from GC-MS (mass spectrometry) data. For reaction conditions in organic solvent see Tables 1 and 2; for reaction conditions in water see Table 3.

Continuous hydrogenation. Palladium-on-carbon (400 mg) suspended in water was poured into a glass column (ϕ = 1 cm) containing a small plug of cotton wool. The top of the column also was stoppered by cotton wool

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TABLE 1

Reduction of Soybean Oil in the Presence of Different Donors and Solvents at Different Temperatures

Donor	Solvent	T (°C)	Reaction
Formic acid	n-Pentane	R.T.[a]	yes[b]
Formic acid	iso-Propanol	R.T.	no[b]
Formic acid	Acetone	R.T.	no[b]
Formic acid	Dimethylformamide	R.T.	no[b]
Formic acid	Dimethylformamide	80	yes[b]
Formic acid	Water	80	yes[b]
Triethylammonium formate	Acetone	R.T.	yes[c]
Triethylammonium formate	Acetone	reflux	yes[c,d]
Sodium formate	Water	R.T.	yes[e]
Sodium formate	Water	80	yes[e]

[a] R.T., room temperature.

[b] Reaction conditions—10 g of soybean oil, 100 mg Pd/C, 25 mL of solvent, 1 mL HCOOH.

[c] Reaction conditions as in Table 2.

[d] Reaction stops after about 2 hr.

[e] Reaction conditions as in Table 3.

TABLE 2

Change in Fatty Acid Composition During Batch Hydrogenation of Soybean Oil in Organic Solvent

Time (hr)	C18:3	C18:2	C18:1	C18:0	C16:0	"iso"[a]	IV	S_L
0	6.9	53.1	23.4	4.5	12.1		129	
0.5	3.5	47.2	32.7	4.5	12.1	3.3	118	3.7
1	3.0	44.5	35.8	4.6	12.1	6.5	115	3.3
2	1.5	40.8	40.9	4.7	12.1	12.2	109	4.0
4	0.4	40.1	42.8	4.6	12.2	16.4	106	6.9
8		29.2	53.6	4.9	12.2	24.2	96	
24		13.1	69.4	5.4	12.1	42.5	81	

[a] Expressed as percent of total fatty acids.

Column: SP-2380 fused silica, 30 m × 0.25 mm ID, 0.25 μm film thickness. Reaction conditions: 5 g of soybean oil, 100 mg Pd/C, 10 mL acetone, 2.3 mL HCOOH, 9.3 mL triethylamine, mechanical stirring, room temperature, 24 hr.

TABLE 3

Change in Fatty Acid Composition During Batch Hydrogenation of Soybean Oil in an Aqueous Medium

Time (hr)	C18:3	C18:2	C18:1	C18:0	C16:0	"iso"[a]	IV	S_L
0	7.5	51.7	24.9	5.4	10.5		130	
1	4.7	48.6	30.7	5.5	10.5	3.7	122	4.0
3	1.9	40.7	41.2	5.6	10.6	8.5	110	3.8
9	0.1	22.0	60.5	7.0	10.5	15.1	89	4.2
24		7.0	74.1	8.4	10.5	33.0	74	
33		1.4	77.3	10.8	10.5	33.1	67	

[a] Expressed as percent of total fatty acids.

Column: FFAP WCOT fused silica, 0.25 mm/50 m. Reaction conditions: 15 g of soybean oil, 110 mg Pd/C, 40 mL NaOOCH 6.5 M, mechanical stirring at 800 rpm, 60°C, 33 hr.

to make an improvised cartridge (flow reactor). An emulsion of 15 g soybean oil in 40 mL of 6.5 M sodium formate was initially formed in an externally stirred 250-mL flask at 800 rpm and continuously pumped through the cartridge by a ProMinent Electronic E Type pump (Chemie und Filter GmbH, Heidelberg, Germany) at a flow rate of 2.5 mL/min for 10 hr. Temperature of the system was held constant between 60 and 80°C. A similar procedure can also be followed with an organic solvent, *e.g.*, acetone, at room temperature.

Methods .of analysis. Fatty acids were determined (quantitated) by GC as methyl esters (FAME) prepared by IUPAC method II.D.19 (15). An SP-2380 fused silica capillary column (30 m × 0.25 mm ID, 0.20 μm film thickness) or a FFAP WCOT fused silica capillary column (50 m × 0.25 mm) was used in a Varian 3400 gas chromatograph (Varian Associates, Palo Alto, CA) equipped with an all-glass splitter system. The GC was operated at 170–210°C, with a heating rate of 4°C/min, and with helium as carrier gas at a flow rate of 1.2 mL/min. The content of "iso" forms, *i.e.*, all positional and geometrical *(trans)* isomers of natural FA obtained during the hydrogenation process, were measured by GC-MS with a Finnigan Mat Ion Trap detector (Sunnyvale, CA) connected to the gas chromatograph. MP and SCI were measured according to AOCS Official Methods Cc 1-25 and Cd 10-57 (16).

The concept of Okkerse *et al.* (17) for initial selectivity (S_L), represented by the scheme Le $\xrightarrow{k_{Le}}$ L $\xrightarrow{k_L}$ O, was adopted. It is assumed that any isomer of Le and L formed during the hydrogenation is as reactive as the Le and L originally present. The following equations are valid for the reaction scheme: $dLe/dt = -k_{Le}[Le]$ and $dL/dt = -k_L[L] + k_{Le}[Le]$ in which [Le] and [L] are the concentrations of Le and L at time, t. S_L is the ratio of the first order reaction constants k_{Le} and k_L: ($S_L = k_{Le}/k_L$).

RESULTS AND DISCUSSION

Preliminary experiments for CTH of soybean oil with Pd/C catalyst are shown in Table 1. The data summarize the reactions with several donors, such as formic acid, triethylammonium and sodium formate, in selected solvents at different temperatures. Initial experiments with triethylammonium formate or sodium formate gave promising results. No reaction was detected with formic acid in isopropanol, acetone or DMF at room temperature, but the reaction proceeded readily at 80°C in water or DMF. When the process with triethylammonium formate in acetone was held at reflux temperature, the reaction terminated after approximately 2 hr. The reason could be a ruined sensitive balance between donor, catalyst and solvent system. These results prompted a thorough investigation of CTH in selected organic solvents and water in the presence of Pd catalyst.

Batch hydrogenation. CTH of soybean oil in acetone with triethylammonium formate at room temperature gave a product with an IV of 81 and a defined fatty acid composition after 24 hr of hydrogenation. The relationship between reaction rate and the fatty acid composition is shown in Table 2. The average initial selectivity (S_L) turned out to be about 4.5, comparable to that obtained in aqueous media as listed in Table 3.

Further experiments were carried out in water with sodium formate as a hydrogen donor at 40 and 60°C. Figure 1 shows that higher temperature obviously enhances the reaction rate and improves the average S_L. The content of "iso" fatty acids was nearly the same after 33 hr of reaction at 60°C as it was after 72 hr of reaction at 40°C. Figure 2 shows that selective reduction to the

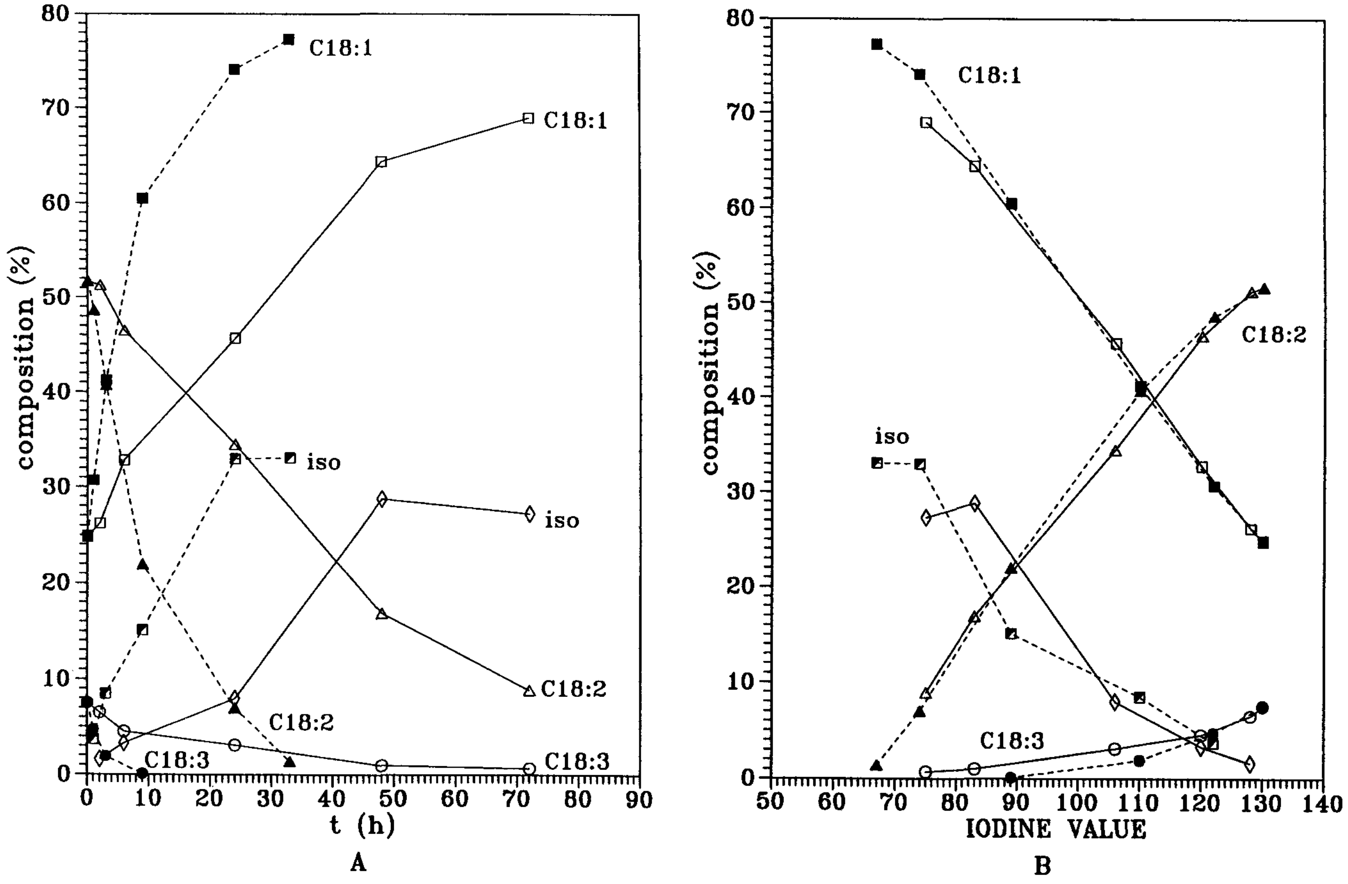

FIG. 1. Changes in fatty acid composition and a portion of the "iso" fatty acids during batch hydrogenation of soybean oil in aqueous medium at 40°C (solid line) and 60°C (broken line). Reaction conditions as described in Experimental Procedures.

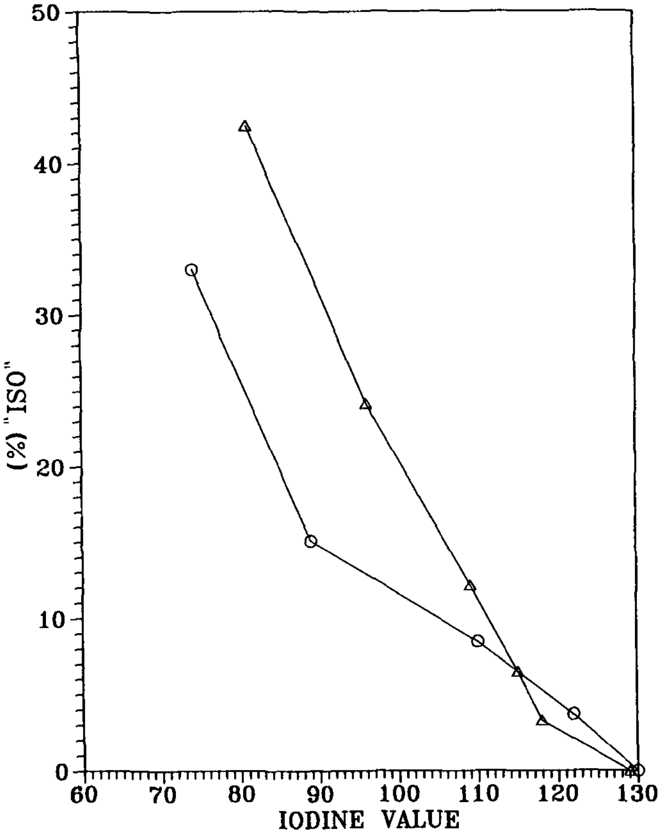

FIG. 2. Yield of the "iso" forms of fatty acids in relation to the method of hydrogenation. Triangle, hydrogenation in an organic solvent (for reaction conditions see Table 2). Circle, hydrogenation in an aqueous medium (for reaction conditions see Table 3).

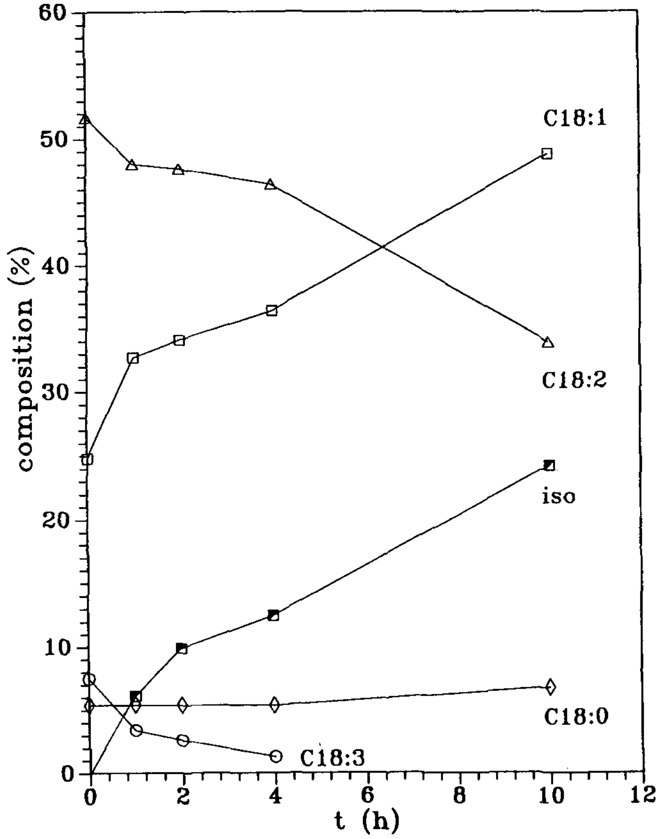

FIG. 3. Changes in fatty acid composition and a portion of the "iso" fatty acids during continuous hydrogenation of soybean oil in an aqueous medium. Reaction conditions as described in Experimental Procedures.

same IV, performed either in an aqueous or in an organic medium, gave significantly lower degrees of isomerization in an aqueous medium. The average S_L at 60°C was 4.0, even better than the reported values of $S_L = 1.3–2.9$ for GH with a catalyst of the same type (5,18); while Arkad (13) reported an S_L value of 5.0 for carrying out CTH on soybean oil methyl esters. This means a small loss of linoleic acid and much faster removal of linolenic acid; the content of the latter was decreased to below 1% after 2 hr, both in solvent and aqueous media (Tables 2 and 3). This is quite an important improvement with regard to the usual manufacture of partially hydrogenated oils by GH. The product, obtained after 33 hr of hydrogenation of soybean oil with sodium formate and Pd/C at 60°C in water, had the following characteristics: IV, 67; MP, 38°C; SCI, 63.4 at 10°C, 60.2 at 15°C, 53.0 at 20°C, 40.8 at 25°C,. 24.7 at 30°C, and 10.8 at 35°C.

CTH offers (through the choice and amount of hydrogen donor) another possibility to control the reaction. The choice of donor affects the reaction *via* its competitive adsorption onto the catalyst, while the choice of the amount of donor permits a simple means of controlling the desired H-level.

Continuous hydrogenation. Recently, Elamin (19) adopted a simple flow reactor for CTH of several olefins, including oleic acid, in the presence of formic acid. We have found that triacylglycerols of soybean oil can be hydrogenated successfully as well by using sodium formate. The catalyst can be reused in the column for an almost unlimited period of time. For a continuous process in an aqueous medium, an emulsion from oil and an almost saturated aqueous solution of sodium formate was prepared, which was later found to be close to the optimum concentration, as reported recently (14). The emulsion had to be stable at the time of flow through the bed of catalyst, where the reaction took place. The emulsion was collected in a stirred vessel after passing the cartridge and was continuously pumped back to the reactor until the desired degree of hydrogenation was attained. The results of the continuous hydrogenation in the described laboratory cartridge is shown in Figure 3.

There are quite a few practical advantages to using CTH with formates, *e.g.*, there is no easily ignited molecular hydrogen, no gas containment, no pressure and no need for high-temperature vessels. Simple stirring of a reaction mixture is usually all that is required. However, we found a disadvantage for both batch and continuous processes carried out in organic solvents—the solvent, the excessive donor and the donor degradation products must be removed from the final product before its application. This problem can be avoided by performing the hydrogenation in an aqueous medium. After completion of the reaction, the aqueous and the oil phases separate, and the water-soluble materials remain in the aqueous phase.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Science, Research and Technology of Slovenia under No. B-723. We thank T. Koloini who provided valuable advice on the continuous process and L. Vidmar who performed MP and SCI analyses.

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[Received August 2, 1991; accepted January 28, 1992]