Microwave-Assisted Catalytic Transfer Hydrogenation of Safflower Oil

B.L.A. Prabhavathi Devi[a], M.S.L. Karuna[a], K. Narasimha Rao[b], P.S. Saiprasad[b], and R.B.N. Prasad[a],*

Departments of [a]Lipid Science & Technology and [b]Catalysis, Indian Institute of Chemical Technology (CSIR), Hyderabad—500 007, India

ABSTRACT: Catalytic transfer hydrogenation (CTH) of safflower oil was studied using aqueous ammonium formate as hydrogen donor and palladium on carbon as catalyst in a closed vessel under controlled microwave irradiation conditions. The method offered good selectivity in complete reduction of linoleic acid to monounsaturated acid with a slight increase in stearic acid compared to other reported catalytic transfer hydrogenation methods. Selectivity was achieved by using microwave-assisted CTH without employing an emulsifier or high ratios of water to oil.

Paper no. J10604 in *JAOCS 80,* 1003–1005 (October 2003).

Edible oils consist mainly of saturated mono-, di-, and tri-unsaturated FA, particularly with a C-18 chain length. Vegetable fats with a semisolid consistency and desired melting characteristics are useful for preparing margarine and special-purpose fats such as high-temperature baking oils. Hydrogenation of edible oils converts liquid oils into semisolid fats with desired melting characteristics and improves oil stability. During traditional partial hydrogenation of soybean oil with molecular hydrogen, the stearic acid content increases up to 30% (1). Monounsaturated FA-rich oils have different organoleptic properties and greater chemical stability and industrial applications than unhydrogenated oils (2).

Selective reduction of linoleic acid in oils such as corn, soybean, and sunflower oils to monounsaturated FA was attempted using a catalytic transfer hydrogenation (CTH) technique (2–5). CTH is a safe, simple, and ecologically friendly method, compared to the conventional catalytic hydrogenation, in which hydrogen gas is replaced with a hydrogen donor. The compounds used as hydrogen donors are easy to store, handle, and transport, unlike pure hydrogen gas under pressure in cylinders. The CHT technique does not require any high-pressure operations and precautionary methods, and can be carried out in a simple vessel without any of the risk associated with using hydrogen gas cylinders.

The commonly used hydrogen donors are cyclohexene, cyclohexadiene, phosphinic acid, hydrazine, formic acid, sodium formate, ammonium formate, and sodium hypophosphite (6). Basu and coworkers (7,8) showed that secondary alcohols also can be used as hydrogen donors, but only under relatively extreme conditions with a reduced selectivity. Formic acid and formic acid salts are efficient hydrogen donors in the presence of a palladium catalyst (9). Arkad *et al.* (3) have studied CTH of FAME prepared from soybean oil in a concentrated aqueous alkali formate solution at 80°C and reported almost complete hydrogenation after 16 h of reaction (3). However, some selectivity toward monounsaturation was also observed at the initial stages. Smidovnic *et al.* (4) carried out CTH of soybean oil with various formic acid salts as hydrogen donors in organic and aqueous media. In organic media the linoleic acid content could not be reduced below 13.1%, with essentially no changes in the content of stearic acid after 24 h, whereas in aqueous medium the linoleic acid content decreased to 1.4% and stearic acid increased from 5.4 to 10.8% after 33 h of reaction time. Smidovnic *et al.* (2) also studied the kinetics of CTH of soybean oil and reported the reduction of only linolenic acid from 7.4 to 1% with a relatively high level of linoleic acid without increase in the stearic acid concentration. Naglic *et al.* (5) studied the CTH of linoleic acid-rich oils such as corn, soybean, and sunflower oils in dilute aqueous sodium formate solution by using 10% Pd/C under atmospheric pressure and observed that the stearic acid content was enriched up to 9.0 to 23.7% from the initial content of 2.8 to 4.7%. In addition, all these reactions were carried out in the presence of an emulsifier, and it is very tedious to remove the emulsifier from the oils after the reaction.

The CTH technique also has been used in conjunction with microwave irradiation for the complete hydrogenation of mono- and diunsaturated FA without any selectivity by using ammonium formate as hydrogen donor in an open vessel in the presence of high-boiling solvents such as ethylene glycol and polar solvents such as methanol, ethanol, and water as the microwave energy transfer agents at about 110–130°C using 10% Pd/C as catalyst (6). Ammonium formate was preferred as hydrogen donor because it decomposes into formic acid and ammonia after the reaction, which can be washed out with water without using any other specific disposal route, whereas the sodium formate-type compounds leave alkali residues in the reaction product.

The aim of the present study was to develop a methodology for the preparation of monounsaturated FA-rich oil from

*To whom correspondence should be addressed at Lipid Science & Technology Division, Indian Institute of Chemical Technology, Hyderabad—500 007, India. E-mail: rbnprasad@iict.res.in

diunsaturated FA-rich safflower oil using a microwave-assisted CTH technique in a closed system without using emulsifier.

EXPERIMENTAL PROCEDURES

Materials. Refined safflower oil was purchased from the local market. The hydrogen donor (ammonium formate) and the catalyst (10% palladium on carbon, Pd/C) were purchased from Merck (Darmstadt, Germany). All the chemicals and solvents were of the highest purity available.

Methods and analysis. The microwave-assisted CTH of refined safflower oil samples was conducted in ETHOS 1600 Microwave Lab Station in batch mode. The FA composition of hydrogenated oils was determined as FAME as prepared by transesterification of the hydrogenated oil using 0.5 M sodium methoxide in methanol for about 30 min at 50°C (10). The analysis of methyl esters was carried out in a gas–liquid chromatograph equipped with an FID by using a stainless steel column (1.8 m × 6 mm) packed with 10% Silar 10C on Chromosorb W-HP (100–120 mesh; Supelco, Bellefonte, PA). The oven temperature was programmed from 180 to 220°C at 5°C per minute, and the flow rate of the carrier gas (nitrogen) was 35 mL/min. The injector and detector temperatures were maintained at 225 and 250°C, respectively, and the area percentage was recorded with a Hewlett-Packard ChemStation data system. The *trans* content of the FAME of the hydrogenated samples was analyzed with an SP2330 column (30 m × 0.25 mm i.d.; Supelco) equipped with an all-gas splitter system and FID with a nitrogen carrier gas flow rate of 1.5 mL/min.

General hydrogenation procedures. Safflower oil (5 g) was placed in a 50-mL Teflon vessel and subjected to microwave irradiation using Microwave Lab Station in the presence of ammonium formate (3, 4, 5, and 6 mol equiv of the oil) as hydrogen donor and 10% Pd/C (0.05–0.25 g, 1 to 5% of oil) in water (0.25–1 mL, 5 to 20% of oil) at 80–160°C and power of 300–600 watt for 20–60 min. The reaction vessel was closed and the hydrogenation carried out. The hydrogenated oil was taken up in chloroform, washed with water, and dried over anhydrous sodium sulfate; chloroform was then removed under reduced pressure.

RESULTS AND DISCUSSION

CTHn of vegetable oils is generally conducted in an open flask with an attached reflux condenser (2–5). Even though some of these reports have described partial selectivity in reduction of PUFA to monounsaturated FA, the reaction conditions, such as use of emulsifier and of a very high ratio of water to oil (100 to 500%), restrict the wide application of these methodologies. The only reference (6) that reported on microwave-assisted CTH describes the complete reduction of oleic and linoleic acids to stearic acid in an unmodified domestic microwave oven. In the present study a Microwave Lab Station was used for the selective reduction of diunsaturated FA-rich safflower oil into monounsaturated FA-rich oil

in a closed system. The selectivity was achieved without using an emulsifier or high ratios of water to oil.

The effect of several chemical and physical parameters was studied to optimize the microwave-assisted CTH procedure for achieving selective reduction of diunsaturated to monounsaturated FA-rich oil.

The catalyst used was 10% Pd/C, and the concentration was varied from 1 to 5% of the substrate. The linoleic acid content was reduced to 42.5 and 7.6% with 1 and 4% of the catalyst, respectively, when the reaction was carried out under optimal reaction conditions. A minimum of 5% catalyst was required for an efficient hydrogenation reaction to convert diunsaturated to monounsaturated FA completely.

Ammonium formate was preferred as hydrogen donor because it decomposes into formic acid and ammonia after the reaction, whereas sodium-formate type compounds leave alkali residues in the reaction product. The choice of the amount of donor is a simple means of controlling the desired hydrogen level (4). Different molar equivalents (3 to 6 with respect to oil) of ammonium formate were used to study the effect of availability of hydrogen to the substrate for selective reduction. Table 1 shows that higher doses of ammonium formate improved the hydrogenation rate. Good selectivity was observed with about 6 equiv of hydrogen donor to convert diunsaturated to monounsaturated FA with very little increase in stearic acid content.

In industrial applications, it is preferable to work with aqueous solutions of hydrogen donors because the unreacted donors and the resulting salt remain in the aqueous phase after workup. In previous reports (2–5), a very high quantity of water (100 to 500% on the basis of substrate) was added in addition to the emulsifier to increase the liquid/liquid interface for better contact of catalyst with the reactants. However, selective hydrogenation was achieved using microwave irradiation with a water content of only 20% on the basis of oil (Table 2). It is also interesting to note that CTH could be conducted without emulsifier when the reaction was carried out using microwave irradiation.

The reaction temperature used for CTH of vegetable oils is usually about 50 to 80°C (2–5). Banik *et al.* (6) in their communication reported the hydrogenation of oleic and linoleic acids to stearic acid in ethylene glycol medium at

TABLE 1
Effect of Ammonium Formate Concentration on Microwave-Assisted CTH of Safflower Oil[a]

Ammonium formate	FA composition (wt%)			
(molar equiv of oil)	16:0	18:0	18:1	18:2
Safflower oil[b]	9.7	2.8	25.3	62.2
3	9.7	4.6	57.5	28.2
4	9.7	4.8	65.0	20.5
5	9.7	5.2	69.5	15.5
6	9.7	5.9	84.4	—

[a]Reaction conditions: 5 g oil, 600 W power, 160°C, 1 h, 20% water, 5% catalyst.
[b]FA composition of unhydrogenated safflower oil. CTH, catalytic transfer hydrogenation.

TABLE 2
Effect of Water Concentration on Microwave-Assisted CTH of Safflower Oil[a]

Water (% of oil)	FA composition (wt %)			
	16:0	18:0	18:1	18:2
Safflower oil[b]	9.7	2.8	25.3	62.2
5	9.7	3.5	65.2	21.6
10	9.7	4.1	71.5	14.7
20	9.7	5.9	84.4	—

[a]Reaction conditions: 5 g oil, 600 W power, 160°C, 1 h, 6 equiv of hydrogen donor, 5% catalyst.
[b]FA composition of unhydrogenated safflower oil. For abbreviation see Table 1.

TABLE 3
Effect of Temperature on Microwave-Assisted CTH of Safflower Oil[a]

Temperature (°C)	FA composition (wt%)			
	16:0	18:0	18:1	18:2
Safflower oil[b]	9.7	2.8	25.3	62.2
80	9.7	3.8	66.8	19.7
100	9.7	4.5	71.5	14.3
120	9.7	5.2	74.6	10.5
140	9.7	5.5	77.0	7.8
160	9.7	5.9	84.4	—

[a]Reaction conditions: 5 g oil, 600 W power, 1 h, 6 equiv of hydrogen donor, 20% water, 5% catalyst.
[b]FA composition of unhydrogenated safflower oil. For abbreviation see Table 1.

TABLE 4
Effect of Time on Microwave-Assisted CTH of Safflower Oil[a]

Time (min)	FA composition (wt%)			
	16:0	18:0	18:1	18:2
0	9.7	2.8	25.3	62.2
15	9.7	3.0	52.9	34.6
30	9.7	5.3	69.4	15.6
45	9.7	5.4	70.4	14.5
60	9.7	5.9	84.4	—

[a]Reaction conditions: 5 g oil, 600 W power, 20% water, 6 equiv of hydrogen donor, 20% water, 5% catalyst.

about 110–130°C using a microwave-assisted CTH reaction. A temperature of 160°C was required for the complete reduction of diunsaturated to monounsaturated FA using microwave-irradiated reaction (Table 3). When quantities of ammonium formate (6 mol equiv of oil), water (20% of oil), and catalyst (5% of oil) were used at the desired levels, the time required for achieving monounsaturated-rich oil was found to be 60 min (Table 4). The *trans* content of the hydrogenated oil was about 43.3% of the monounsaturated FA and is less than or comparable to that of the values of conventional partially hydrogenated vegetable oil (the ratio of *trans* to *cis* is 4:1) and CTH of soybean oil (38%).

ACKNOWLEDGMENTS

REFERENCES

1. Robert, C.H., Hydrogenation, in *Bailey's Industrial Oil and Fat Products,* 5th edn., edited by Y.H. Hui, John Wiley & Sons, 1996, Vol. 4, pp. 213–299.
2. Smidovnik, A., J. Kobe, S. Leskovsek, and T. Koloini, Kinetics of Catalytic Transfer Hydrogenation of Soybean Oil, *J. Am. Oil Chem. Soc. 71:*507–511 (1994).
3. Arkad, O., H. Wiener, N. Garti, and Y. Sasson, Catalytic Transfer Hydrogenation of Soybean Oil Methyl Esters Using Inorganic Formic Acid Salts as Donors, *Ibid. 64:*1529–1532 (1987).
4. Smidovnik, A., A. Stimac, and J. Kobe, Catalytic Transfer Hydrogenation of Soybean Oil, *Ibid. 69:*405–409 (1992).
5. Naglic, M., A. Smidovnik, and T. Koloini, Kinetics of Catalytic Transfer Hydrogenation of Some Vegetable Oils, *Ibid. 75:* 629–633 (1998).
6. Banik, B.K., K.J. Barakat, D.R. Wagle, M.S. Manhas, and A.K. Bose, Microwave-Assisted Rapid and Simplified Hydrogenation, *J. Org. Chem. 64:*5746–5753 (1999).
7. Basu, H.N., and M.M. Chakrabarty, Studies on Conjugated Hydrogenation: Nickel Catalyst with Alcohols, *J. Am. Oil Chem. Soc. 43:*119–121 (1966).
8. Chakrabarty, M.M., D. Bhattacharyya, and A.K. Basu, Conjugated Hydrogenation of Triglyceride Oil Containing Conjugated Acid, *Ibid. 49:*510–514 (1972).
9. Marcec, R., Catalytic Hydrogenation of Some Organic Halides by Hydrogen Transfer from Lithium Formate in the Presence of Ruthenium and Rhodium Complexes, *Croat. Chem. Acta 63:*203–206 (1990).
10. Christie, W.W., The Preparation of the Alkyl Esters from Fatty Acids and Lipids, in *Topics in Lipid Chemistry,* edited by F.D Gunstone, Paul Elek (Scientific Books), London, 1972, Vol. 3, pp. 171–198.