The Electrochemical Hydrogenation of Edible Oils in a Solid Polymer Electrolyte Reactor. I. Reactor Design and Operation

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ABSTRACT: A new electrochemical method has been devised and tested for the moderate temperature/atmospheric pressure hydrogenation of edible oils, fatty acids, and fatty acid methyl esters. The method employed a solid polymer electrolyte (SPE) reactor, similar to that used in H_2/O_2 fuel cells, with water as the source of hydrogen. The key component of the reactor was a membrane-electrode-assembly, composed of a RuO_2 powder anode and either a Pt-black or Pd-black powder cathode that were hot-pressed as thin films onto the opposing surfaces of a Nafion cation-exchange membrane. During reactor operation at a constant applied current, water was back-fed to the RuO_2 anode, where it was oxidized electrochemically to O_2 and H^+. Protons migrated through the Nafion membrane under the influence of the applied electric field and contacted the Pt or Pd cathode, where they were reduced to atomic and molecular hydrogen. Oil was circulated past the back side of the cathode and unsaturated triglycerides reacted with the electrogenerated hydrogen species. The SPE reactor was operated successfully at a constant applied current density of 0.10 A/cm^2 and a temperature between 50 and 80°C with soybean, canola, and cottonseed oils and with mixtures of fatty acids and fatty acid methyl esters. Reaction products with iodine values in the range of 60–105 were characterized by a higher stearic acid content and a lower percentage of *trans* isomers than those produced in a traditional hydrogenation process.
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KEY WORDS: Canola oil, cottonseed oil, current efficiency, fatty acid mixtures, Pd-black, Pt-black, soybean oil, *trans* isomers, triacylglycerol.

Hydrogenation of the unsaturated fatty acid constituents of an edible oil's triglycerides is carried out to produce a more oxidatively stable product and/or to change a normally liquid oil into a semisolid or solid fat. Most commercial oil hydrogenation plants use Raney or supported nickel catalyst, and the reaction is carried out at a high temperature (typically 150–225°C) and a hydrogen gas pressure in the range of 10–60 psig (1). These conditions are required to increase the solubility of hydrogen gas in the oil/catalyst reaction medium and to accelerate the hydrogenation reaction rate on the catalyst surface. Unfortunately, high reaction temperatures promote oil degradation and other deleterious side reactions, including the undesirable production of *trans* fatty acid isomers (2).

An alternative method for edible oil hydrogenation is a low-temperature electrocatalytic route, where an electrically conducting catalyst (e.g., Raney nickel or platinum black) is used as the cathode in an electrochemical reactor. Atomic hydrogen is generated on the catalyst surface by the reduction of protons or water molecules in the electrolytic reaction medium. The electrogenerated hydrogen then reacts chemically with unsaturated fatty acids in the oil's triglycerides. The overall oil hydrogenation reaction sequence is as follows:

$$2H^+ + 2e^- \rightarrow 2H_{ads} \qquad [1]$$

$$2H_{ads} + \text{R-CH=CH-R}' \rightarrow \text{R-CH}_2\text{-CH}_2\text{-R}' \qquad [2]$$
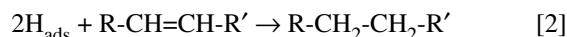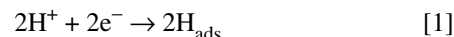
An unwanted side reaction, which consumes current but does not affect the product yield, is the formation of H_2 gas, either by the chemical combination of two adsorbed hydrogen atoms or by the electrochemical reduction of adsorbed hydrogen,

$$2H_{ads} \rightarrow H_2 \text{ (gas)} \qquad [3]$$

$$H_{ads} + H^+ + e^- \rightarrow H_2\text{(gas)} \qquad [4]$$
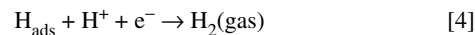
Unlike a chemical catalytic oil hydrogenation process, the predominant reaction for supplying hydrogen to the catalyst surface is Equation 1, and not the dissociation of H_2 to $2H_{ads}$ (i.e., when electrons are pumped into a cathode, there is essentially no production of atomic hydrogen from H_2).

All electrochemical reactors must contain two electrodes, a cathode for reduction reactions and an anode at which one or more oxidation reactions occur. For a water-based electrolytic solution, the anode reaction is usually the oxidation of H_2O,

$$H_2O \rightarrow {}^1\!/_2O_2 + 2H^+ + 2e^- \qquad [5]$$
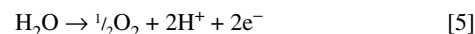
Edible oil hydrogenation is a particularly attractive reac-

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tion to examine in an electrocatalytic scheme. The hydrogen concentration on the catalyst surface can be controlled by the applied current, in which case the reactor temperature and pressures can be lowered and unwanted isomerization and thermal degradation reactions can be minimized. Normally, only 25–50% of the double bonds in an oil are hydrogenated, thus eliminating the common problem in electrochemical reactors of high H_2 evolution rates when the unsaturated starting material is nearly depleted. Also, the high molecular weight of the starting oil (892 g/mole for refined soybean oil) means that the electrical energy consumption per pound of hydrogenated product will be low, even though the saturation of a double bond requires 2 F/mole of electron charge.

Numerous studies have shown that low hydrogen overpotential electrically conducting catalysts (e.g., Raney nickel, platinum and palladium on carbon powder, and Devarda copper) can be used to electrocatalytically hydrogenate a variety of organic compounds, including benzene and multi-ring aromatic compounds, phenol, ketones, nitrocompounds, dinitriles, and glucose (3–10). These reactions were carried out in both batch and semicontinuous flow reactors; in most reactions, the products were similar to those obtained from a traditional chemical catalytic scheme at elevated temperatures and pressures.

Yusem, Pintauro, and coworkers (11–13) have shown that soybean oil can be hydrogenated electrocatalytically at a moderate temperature (70–75°C) and one atmosphere pressure in flow-through packed-bed reactors, without an external supply of pressurized H_2 gas. The reaction medium was a two-phase mixture of soybean oil in a water/*t*-butanol solvent that contained tetraethylammonium *p*-toluenesulfonate as the supporting electrolyte. Hydrogenation current efficiencies (CE) (a direct measure of the oil hydrogenation rate as compared to the total rate of atomic hydrogen production) in the range of 50–100% were obtained for apparent current densities of 1.0×10^{-2} to 2.0×10^{-2} A/cm^2 and an oil concentration between 20 and 40%. The electrohydrogenated oil was characterized by a somewhat higher stearic acid content and a lower percentage of *trans* fatty acid isomers, as compared to the products from a traditional high-temperature hydrogenation process.

A serious drawback of the electrochemical Raney nickel reactor work was the use of a nonfood-grade co-solvent (*t*-butanol) and supporting electrolyte (tetraethylammonium *p*-toluenesulfonate), which were needed to stabilize the emulsified oil/water reaction medium and to achieve a reasonable ionic conductivity in the water/alcohol phase. In the present study, this problem has been circumvented by use of a solid polymer electrolyte (SPE) reactor for oil/fatty acid hydrogenation, where a hydrated polymeric cation-exchange membrane carries out the function of the solvent/supporting electrolyte. Preliminary edible oil and fatty acid hydrogenation data in an SPE reactor with a platinum or palladium catalyst cathode and water as the source of hydrogen are the subject matter of this paper.

Background on solid polymer electrolyte reactors. A solid polymer electrolyte reactor for organic species hydrogenation consists of separate anode and cathode chambers that are separated by a thin, hydrated cation-exchange membrane. Precious metal catalyst powder electrodes (one anode and one cathode) are fixed to opposing faces of the membrane, forming a "membrane-electrode-assembly" (MEA) similar to that employed in SPE hydrogen/oxygen fuel cells. Water is circulated past the back side of the anode, where water molecules are oxidized to O_2 gas and protons, according to Equation 5 (alternatively, H_2 gas can be oxidized to two protons and two electrons at the anode). The protons from H_2 or H_2O oxidation then migrate through the ion-exchange membranes under the influence of the applied electric field to the cathode catalyst component of the MEA, where the protons are reduced to atomic and molecular hydrogen (Equations 1 and 3). This electrogenerated hydrogen can then react with unsaturated fatty acids of an edible oil, where the oil is circulated through the cathode chamber and flows past the back side of the cathode (in effect, the oil hydrogenation reaction occurs within the MEA at a three-phase interface where oil, water, and catalyst meet). The principles of operation for an SPE reactor during edible oil operation are summarized in Figure 1. Ion (proton) conductivity between the anode and cathode occurs through the wetted cation-exchange membrane, so that pure oil and distilled water (or H_2 gas) can be circulated in the cathode and anode chambers, respectively. In this regard, the SPE reactor represents a significant improvement over our prior electrochemical reactor studies because inorganic salts and organic solvents that can contaminate the oil are not needed. The close proximity of the anode and cathode on an MEA (the electrodes are separated by the ion-exchange membrane, which is at most 200 µm in thickness) and the high ion-exchange capacity of the cation-exchange membrane ensures facile H^+ transport between the anode and cathode.

SPE reactors have been examined previously for organic electrochemical syntheses (both oxidation and reduction re-
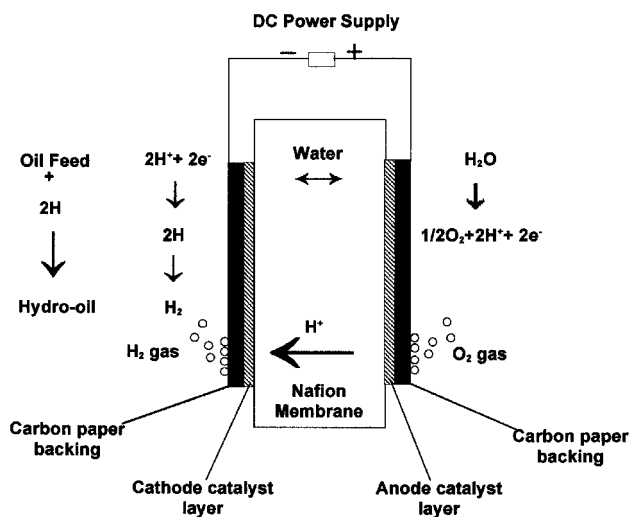

FIG. 1. Principles of operation of a solid polymer electrolyte (SPE) reactor during the electrohydrogenation of an oil.

actions). Most of the published work on reduction reactions was carried out by Ogumi and co-workers who studied, for example, the electrohydrogenation of nitrobenzene to aniline by using a Cu-Pt cathode/Nafion® membrane/Pt anode MEA (14) and the reduction of cyclooctene, α-methyl stylene, and diethyl maleate at a Pt cathode/Nafion® membrane/Pt anode MEA (15) (Nafion is a registered trademark of E.I. DuPont de Nemours & Co., Inc., Wilmington, DE).

EXPERIMENTAL PROCEDURES

MEA. The key component of the SPE reactor was an MEA which was composed of catalytic powders that were hot-pressed as thin films onto the opposing surfaces of a cation-exchange membrane (in the present study, a Nafion 117 perfluorosulfonic acid cation-exchange membrane was employed). The cathode was prepared by: (i) mixing thoroughly a noble metal catalyst powder (either Pt-black or Pd-black, from Aldrich Chemical Co., Milwaukee, WI) with dispersions of 5 wt% Nafion in isopropanol and Teflon-30, a PTFE/isopropanol dispersion (both were purchased from ElectroChem, Inc., Woburn, MA); (ii) coating one surface of a 2.0×2.0 cm carbon paper sheet (Toray carbon paper with a thickness of 0.0067 in.) with the catalyst/polymer solution; and (iii) heating the carbon paper to 100°C for 1 h to evaporate the isopropanol solvent. The cathode catalyst loading was fixed at 2.0 mg/cm^2 (with a catalyst thickness ≤ 0.1 mm), and the amounts of Nafion and Teflon polymers (which acted as binders for the metal powder catalyst) were both fixed at 10 wt% (based on the dry catalyst weight). The anode used in this study was composed of RuO_2 powder mixed with 20 wt% Nafion and 15 wt% PTFE (dry catalyst weight-basis). The general procedure for anode fabrication (coating on carbon paper and heating to remove alcohol solvent) was similar to that for the cathode, but the RuO_2 loading was fixed at 2.5 mg/cm^2. RuO_2 is the catalyst of choice for electrochemical water oxidation to O_2 because of its good catalytic activity and mechanical stability. After the coating procedure, the carbon paper anode and cathode were hot-pressed onto the opposing faces of a Nafion 117 membrane (at a pressure of 160 atm and a temperature of 250°F, or 121°C, for 90 s).

Experimental reactor. Hydrogenation reactions were carried out in the SPE reactor, shown schematically in Figure 2. The reactor was constructed of two stainless steel halves, each containing grooved feed channels that provided both mechanical support and electrical contact for the MEA (to eliminate metal corrosion, the anode feed channel was constructed of titanium). The MEA was secured tightly between the cathode and anode flow channels with silicon gaskets and stainless steel bolts.

The SPE reactor was operated in a batch recycle mode by insertion into a circulation loop, consisting of anolyte and catholyte peristaltic pumps and holding tanks immersed in a constant-temperature oil bath (see Fig. 3). Oil (or a fatty acid mixture) and deionized distilled water were continuously and separately circulated past the back sides of the cathode and
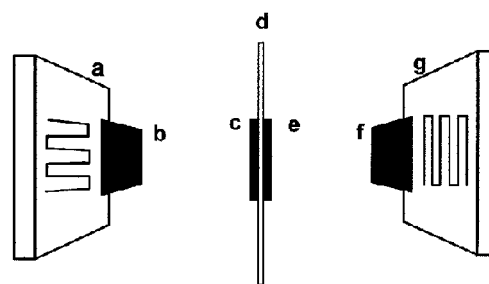

FIG. 2. Schematic diagram of the SPE reactor. (a,g) Reactor blocks with cross-patterned flow field; (b) gas/oil permeable backing, cathode side; (c) cathode thin-film catalyst layer; (d) Nafion cation-exchange membrane; (e) anode thin-film catalyst layer; (f) gas/water permeable backing, anode side. For abbreviation see Figure 1.

anode, respectively, at a flow rate of 80 mL/min. The hydrogenation reactor was operated at a constant current density of 0.10 A/cm^2 with equal amounts of oil and water (between 10 and 30 g per experiment). Electrolyses were carried out with: (i) refined and bleached soybean oil, (ii) refined, bleached, and dewaxed canola oil, (iii) refined, bleached, deodorized, and winterized cottonseed oil (all three were provided by Lou Ana Foods Division of Ventura Food, LLC, Opelousas, LA), (iv) a C_{18} fatty acid mixture provided by Archer Daniels Midland Company (Decatur, IL), and (v) a prepared mixture of methyl oleate (99%) and methyl linoleate (99%) that were purchased from Aldrich Chemical Co. Reaction temperatures, which ranged from 50 to 80°C, were achieved by heating the oil and water holding tanks and attaching resistance heaters to the reactor's outer surface.

Product analyses. For each experiment, the oil or fatty acid mixture reactant and hydrogenated products were analyzed for: (i) fatty acid composition [gas chromatography (GC)
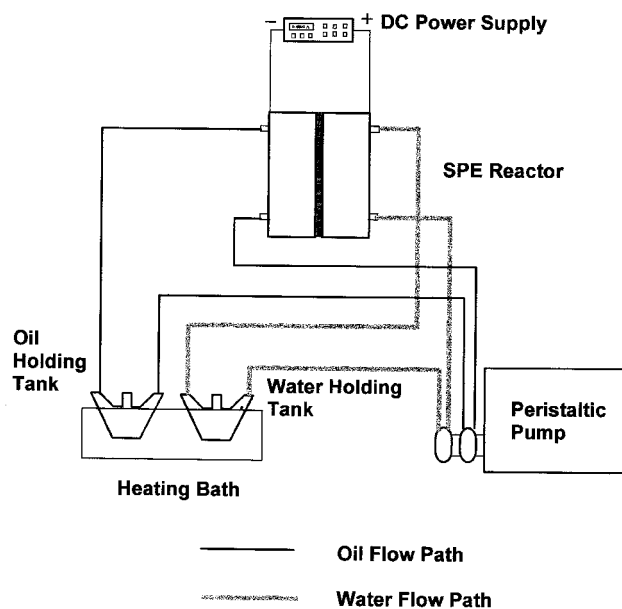

FIG. 3. Batch recycle apparatus for the electrohydrogenation experiments. For abbreviation see Figure 1.

analysis of fatty acid methyl esters, according to AOCS methods (16) Ce 1-62 and Ce 2-66], (ii) iodine value (IV: calculated directly from the GC fatty acid composition according to AOCS method Cd 1c-85), (iii) peroxide value (AOCS method Cd 8-53), (iv) total *trans* isomers, either from the gas chromatograms or by a Fourier transform infrared analysis (AOCS method Cd 14-61), and (v) free fatty acid (AOCS method Ca 5a-40). Triacylglycerol analyses were also performed by high-performance liquid chromatography as has been described previously (17).

The efficiency of electrogenerated hydrogen addition to fatty acid double bonds was gauged by the oil hydrogenation CE, which was computed from the change in total moles of double bonds in the oil/fatty acid reactant (as determined from the GC fatty acid profiles of reactant and final product samples) and the total charge passed in an electrolysis (the product of the applied constant current and time-duration of an experiment),

$$ CE\ (\%)\ =\ 100 \cdot \left[\frac{\Delta\ \text{moles of double bonds}}{(2\ \text{equiv/mol})\ QF} \right] \qquad [6] $$

where *F* is Faraday's constant (96,487 C/equiv), and *Q* is the total charge passed during a hydrogenation experiment (with units of coulombs). In the present reaction scheme, cathode CE of less than 100% were attributed solely to H_2 gas evolution, according to Equations 3 and/or 4. As is normally done in organic electrochemical synthesis, a specified charge was passed in each oil hydrogenation experiment and the product oil IV varied depending on the hydrogenation CE.

RESULTS AND DISCUSSION

Representative data for soybean oil electrohydrogenation in an SPE reactor with either a Pt or Pd cathode catalyst are given in Tables 1 and 2 for an oil product IV that ranged from about 60 to 100. All of these electrolyses were carried out at 60°C, with a constant current density of 0.1 A/cm². The electrochemical performance of the SPE reactor was good, with oil hydrogenation CE in the range of 40 to 65%. In almost all experiments, a Pd-black cathode gave higher CE, as would be expected because its catalytic activity is higher than that of Pt (18,19), i.e., when the reaction of H and oil on the catalyst surface was fast, the surface concentration of atomic hydrogen remained low, thus minimizing the hydrogen gas evolution reaction. Although oil hydrogenation CE in our previous studies with a Raney nickel powder cathode were higher than those in the present study (as high as 80 to 100%), the current density was one order of magnitude lower than that employed with the SPE reactor. A low operating current density for an electrocatalytic hydrogenation reactor is not desirable, even if the CE for hydrogen utilization by the organic substrate is high. From an oil processing viewpoint, the production rate of a hydrogenated oil with a specified IV in reactors of equal cathode area will scale directly with the product of current density and CE. Thus, an SPE reactor operating at 0.10 A/cm² and 50% CE will produce five times as much of the same hydrogenated oil as a Raney nickel reactor at 0.010 A/cm² and 100% CE.

The values of the anode–cathode voltage drop in Tables 1

TABLE 1
Solid Polymer Electrolyte (SPE) Reactor Performance with Refined Bleached (RB) Soybean Oil and a Pt-Black Cathode[a]

	Fatty acid profile (area%)				IV[b]	SLn	SLo	So	Voltage drop (V)	CE (%)	% *Trans*
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$							
Starting oil	4.0	22.5	54.6	7.7	134						0
Exp. #1	19.7	24.5	39.8	4.5	102	1.4	0.58	0.81	1.65	40	3.8
Exp. #2	28.4	21.3	34.8	4.2	90	1.1	0.49	0.56	1.85	55	2.8
Exp. #3	32.7	23.5	29.5	2.7	78	1.2	0.60	0.71	1.55	40	
Exp. #4	38.7	22.4	24.9	2.2	68	1.2	0.63	0.71	1.55	48	3.5

[a]RuO₂ anode, 60°C reactor temperature, 1 atm reactor pressure, 0.10 A/cm² current density.
[b]IV, iodine value; Sln, linolenate selectivity; SLo, linoleate selectivity; So, oleate selectivity; CE, current efficiency.

TABLE 2
SPE Reactor Performance with RB Soybean Oil and a Pd-Black Cathode[a,b]

|	Fatty acid profile (area %)				IV[b]	SLn	SLo	So	Voltage drop (V)	CE (%)	% *Trans*
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$							
Starting oil	4.0	22.5	54.6	7.7	134						0
Exp. #1	23.8	28.9	32.5	3.6	91	1.24	0.84	1.04	1.65	52	6.5
Exp. #2	28.1	31.7	26.2	2.7	80	1.2	1.06	1.29	1.65	65	
Exp. #3	37.4	26.9	22.2	1.7	66	1.4	0.87	1.24	1.55	53	7.4
Exp. #4	37.4	32.3	17.9	1.0	62	1.57	1.24	1.95	1.65	49	8.0

[a]RuO₂ anode, 0.10 A/cm² current density, 60°C reactor temperature.
[b]See Table 1 for abbreviations.

and 2 are low and only 0.32–0.62 V greater than the thermodynamic potential needed to generate O_2 from water at the anode and H_2 from H^+ at the cathode. The added cell voltage observed in the experiments was due to the finite electrical resistance of the ion-exchange membrane that separated the anode and cathode and additional energies that are needed to overcome kinetic limitations at the two electrodes (the so-called anodic and cathodic activation overpotentials). The total power requirement of the SPE reactor for oil hydrogenation was directly proportional to the current, voltage, and degree of oil saturation, and inversely proportional to the hydrogenation current efficiency. Thus, for an SPE reactor that produced an IV 91 soybean oil and operated at 0.10 A/cm^2, 1.65 V, and a CE of 52% (*cf.* Exp. #1 in Table 2), the power requirement for both generating hydrogen from water and hydrogenating the oil was 0.13 kw-h/lb of oil, which translated into an energy cost of $0.0091/lb (at $0.07/kw-h).

Only the C_{18} fatty acids are listed in Tables 1 and 2; we found no change in the other fatty acids (e.g., $C_{16:0}$ and $C_{20:0}$) over the course of a hydrogenation experiment. Also, the peroxide value of the oil products in Tables 1 and 2 (as well as in all subsequent SPE experiments) was <2.0 and usually less than 1.0. Although O_2 gas was generated in close proximity to the oil (at the anode face of the MEA), it did not contact the oil because diffusion of O_2 through the cation-exchange membrane of the MEA was slow and because any O_2 that did penetrate through the membrane was quickly reduced electrochemically to water at the cathode catalyst. Contact of oil with water within the MEA did not result in triglyceride hydrolysis, as evidenced by free fatty acids levels of 0.03–0.04 in refined/bleached and electrochemically hydrogenated soybean oil samples (the low operating temperature of the reactor probably minimized free fatty acid formation).

From a close inspection of the fatty acid profiles in Table 1 and 2, it was clear that: (i) the hydrogenated oil products from the SPE reactor contained more stearic and linolenic acids, as compared to the products from the high-temperature chemical catalytic hydrogenation of soybean oil with Raney nickel (1); and (ii) oil products from the Pd-black cathode electrolyses had somewhat less $C_{18:0}$ and $C_{18:3}$, as compared to those at a Pt cathode for a similar IV. The high saturated fat ($C_{18:0}$) content in the SPE hydro-oils was attributed to the use of Pt and Pd cathode catalysts. The difference in selectivity between a Pt and Pd cathode was in good agreement with our general understanding of hydrogenation selectivity as a function of catalyst type (18,19). To interpret and compare the fatty acid profiles in Tables 1 and 2, the linolenate, linoleate, and oleate selectivities (denoted as SLn, SLo, and So, respectively) were computed. These selectivities were based on the following simplified reaction sequence for the hydrogenation of C_{18} fatty acids in soybean oil:

$$\text{linolenate} \xrightarrow{k_1} \text{linoleate} \xrightarrow{k_2} \text{oleate} \xrightarrow{k_3} \text{stearic} \qquad [7]$$
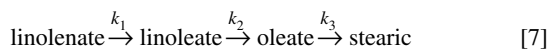
The relative rates of the individual reactions were quantitated in terms of three selectivities,

$$\text{SLn} = \frac{k_1}{k_2}; \quad \text{SLo} = \frac{k_2}{k_3}; \quad \text{So} = \frac{k_1}{k_3} \qquad [8]$$

The rate constants in the above equations were determined by combining the fatty acid compositions of the starting oil and final product, for a given SPE reactor experiment, with the following first-order rate expressions:

$$\frac{d[\text{oleate}]}{dt} = k_2[\text{linoleate}] - k_3[\text{oleate}]$$

$$\frac{d[\text{linoleate}]}{dt} = k_1[\text{linolenate}] - k_2[\text{linoleate}] \qquad [9]$$

$$\frac{d[\text{linolenate}]}{dt} = -k_1[\text{linolenate}]$$

Soybean oil fatty acid selectivities in the SPE reactor were comparable to those from chemical catalytic hydrogenations in a slurry reactor with H_2 gas and a Pt/Al_2O_3 catalyst, where SLn = 1.35 and SLo = 0.85 at 60°C and 145 psig (20). On the other hand, the SPE selectivities were not as high as those from a Pd/C or nickel catalyst slurry reactor. For example, SLn = 2.9 and SLo = 13.5 at 60°C and 145 psig with a Pd/C catalyst (20), SLn = 1.3 and SLo = 2.6 at 70°C and 400 psig with Pd/Al_2O_3 (21), and 1.5 < SLn < 2–3 and 5 < SLo < 100 with a Raney nickel catalyst at 127–192°C and 7–73 psig (19). The low selectivities in the Pd-cathode reactor, as compared to slurry reactor results, have been tentatively attributed to slow mass transfer of triglycerides to and from catalytic sites within the MEA structure (oil molecules must diffuse through the carbon paper backing and into the Nafion/PTFE binder in order to reach catalytic sites where atomic hydrogen is electrochemically generated). Such mass transfer limitations played no role when a less-active Pt catalyst was employed in the SPE reactor. The effect of mass transfer in an MEA on oil hydrogenation selectivities was not intuitively obvious because: (i) the location of the reaction zone within the MEA, where oil, catalyst, electrons, and H^+ meet, was not known, and (ii) the interaction(s) of diffusing triglycerides with the Nafion and PTFE catalyst binders were not known. Additional studies on the interdependence of mass transfer, catalyst type, and MEA construction on oil hydrogenation selectivities is currently underway and will be the subject of a future publication.

SPE reactor performance data for reaction temperatures in the range of 50–80°C are listed in Table 3 for a Pt-black or Pd-black cathode. The product IV varied from 85 to 114, depending on the total charge passed during an electrolysis and the CE for oil hydrogenation. A 50°C experiment could not be carried out with a Pt-black cathode because the anode/cathode voltage drop quickly rose to an unacceptably high level after the current was applied. We have tentatively attributed this finding to the preferential synthesis of high-melting saturated triglycerides (e.g., tristearin) that coated the Pt-catalyst surface. In general, we found that variations in reaction temperature for $60 \leq T \leq 80$°C had little effect on the fatty acid hydrogenation selectivities and CE. A significant improvement in selectivity was observed for a 50°C electrolysis with

TABLE 3
SPE Reactor Performance with RB Soybean Oil at Different Reaction Temperatures

	Catalyst	Fatty acid profile (area %)				IV^b	SLn	SLo	So	CE (%)	% *Trans*
		$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$						
Starting oil		4.0	22.5	54.6	7.7	134					0
50°C	Pt^c										
	Pd	9.1	41.7	34.7	3.3	105	1.54	3.60	5.53	36	10.5
60°C	Pt	19.7	24.5	39.8	4.5	102	1.40	0.58	0.81	40	1.3
	Pd	25.6	30.7	29.7	2.9	85	1.35	0.96	1.30	59	7.7
70°C	Pt	18.5	24.3	41.1	4.6	104	1.22	0.58	0.70	41	0.0
	Pd	25.2	30.7	30.2	2.8	86	1.43	0.96	1.37	58	8.4
80°C	Pt	13.0	24.8	45.5	5.3	114	1.23	0.62	0.76	28	0.8
	Pd	24.3	31.4	30.0	3.0	92	1.33	1.01	1.34	56	7.5

^{a}RuO$_2$ anode, 0.10 A/cm^2 current density, 1 atm reactor pressure.
^{b}An oil hydrogenation experiment could not be carried out at 50°C with a Pt catalyst cathode. See Table 1 for abbreviations.

a Pd-black cathode, although the CE was somewhat lower than that from higher-temperature Pd experiments. The high values of SLn, SLo, and So at 50°C are consistent with a reaction mechanism such as that shown in Equation 7, where the decrease in rate constant with temperature is not the same for the various hydrogenation steps from linolenate to stearate (i.e., k_3 decreases more than k_1 and k_2 with decreasing temperature).

Perhaps the single most important finding from the SPE reactor experiments with soybean oil was the low *trans* isomer content of the oil products. *Trans* fatty acids are known to affect the physical and nutritional properties of edible oils. *Trans* isomers have high melting points that can influence the liquid/solid characteristics of the hydro-oil, and human health-effect studies have indicated that *trans* fatty acid isomers raise blood levels of harmful low-density lipoprotein cholesterol while lowering protective high-density lipopro-

tein levels (22). In general, we found that the *trans* isomer content of hydrogenated oil products from the SPE reactor was always low (below 10%), with significantly less *trans* isomer formation when a Pt-black cathode was employed. The percentage of *trans* isomers formed at a Pt-black cathode remained below 4% for a product IV in the 66–115 range, while the *trans* isomer content with a Pd cathode was somewhat higher at 6.5–10.5% for oil IV of 61–105. The low *trans*

TABLE 4
Triacylglycerol Analyses of Soybean Oil and Hydrogenated Soybean Oils^a

		HSBO	
TAG	SBO	80°C/Pd cathode	50°C/Pd cathode
LnLnL	0.8	0.3	0.3
LnLL	6.4	2.9	3.1
LnLnO	0.4	0.5	0.2
LnLnP	0.1	0.3	0.1
LLL	18.0	9.0	10.0
LnLO	5.3	3.2	3.1
LnLP	3.1	1.3	1.3
LLO	16.4	10.2	12.1
LnOO	1.4	1.6	2.0
LLP	13.2	8.0	8.8
LnOP	2.1	1.4	1.1
LnPP	0.6	0.1	0.0
LOO	6.9	5.4	7.2
LLS	3.7	3.5	4.6
LOP	8.6	7.8	8.9
PLP	2.4	1.5	1.7
OOO	2.6	3.0	5.4
LOS	2.7	4.6	8.7
POO	2.0	4.9	8.0
SLP	1.3	3.6	4.9
POP	0.7	1.3	1.8
SOO	0.7	0.9	1.3
SLS	0.3	1.2	1.6
SOP	0.4	0.0	1.0
PPS	0.0	0.6	0.0
SOS	0.0	2.4	0.4
PSS	0.0	7.0	0.9
SSS	0.0	13.3	1.9

^{a}TAG, triacylglycerol; SBO, soybean oil; HSBO, hydrogenated soybean oil; L, linoleate; Ln, linolenate; O, oleate; P, palmitate; S, stearate.
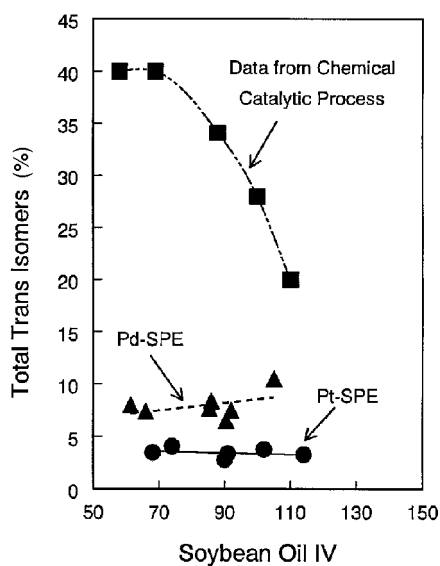

FIG. 4. Comparison of the total *trans* isomer content vs. soybean oil product iodine value (IV) for the SPE reactor and for a high-temperature chemical catalytic hydrogenation method. For chemical catalytic hydrogenation data, see (1). For abbreviation see Figure 1.

TABLE 5
SPE Reactor Performance and Chemical Properties of Electrohydrogenated Canola Oil[a]

	Fatty acid profile (area %)					%				Voltage	CE
	$C_{18:0}$	$C_{18:0}$	$C_{18:2}$	$C_{18:3}$	IV	Trans	SLn	SLo	So	drop (V)	(%)
Starting oil	1.4	60.1	21.2	11.3	118.0	0					
Pt cathode	10.1	56.1	19.6	9.3	107	0	1.10	1.35	1.49	1.65	9.7
Pd cathode	15.6	57.5	16.3	6.1	94	2.8	1.15	2.50	2.86	1.65	41.4

[a]RuO_2 anode, 60°C reactor temperature, 1 atm reactor pressure, 0.10 A/cm^2 current density. See Table 1 for abbreviations.

fatty acid production rates were attributed to the combined effects of a low operating temperature of the SPE reactor (60–80°C) and the use of a precious metal catalyst cathode. According to the GC analysis of fatty acid methyl esters, *trans* isomers were concentrated in the *trans* $C_{18:1}$ fatty acids. The *trans* isomer data in Tables 1–3 for Pt-black and Pd-black cathodes are summarized in Figure 4, where the % *trans* is plotted vs. the oil product IV. This figure also shows *trans* data for the chemical catalytic hydrogenation of soybean oil with Raney nickel (1). The improvement in *trans* content for the SPE reactor oil products is obvious. The *trans* isomer content of soybean oil hydrogenated in the SPE reactor was somewhat lower than that for oils processed in a pressurized chemical catalytic reactor with Pd or Pt. For example, the *trans* fatty acid content of an IV 102 soybean oil was reported to be 20% for a slurry reactor with a Pd/C catalyst that was operated at 60°C and 145 psig (22); the corresponding *trans* content for an IV 102 oil in a Pd cathode SPE reactor was 8.5%. Similarly, the *trans* content of a chemically hydrogenated IV 102 soybean oil (with a Pt/Al$_2$O$_3$ catalyst and operating at 60°C and 145 psig) was 5.4% (22), as compared to 3.8% *trans* for the same IV oil product from a Pt-cathode SPE reactor experiment. It should be noted with regard to Figure 4 that nickel catalysts are known to be more selective than either Pt or Pd for soybean oil hydrogenation. Nevertheless, the sum of the total *trans* isomers and saturated 18-carbon fatty acids produced in the SPE reactor was less than that synthesized in a traditional chemical catalytic hydrogenation scheme with Ni. Using an IV 90 soybean oil as an example, the total $C_{18:0}$ plus *trans* content was found to be 41% for a Ni catalyst (35% *trans* and 6% $C_{18:0}$) (1), 31.2% for a Pt catalyst in the SPE reactor (2.8% *trans* and 28.4% $C_{18:0}$), and 30.3% for a Pd catalyst in the SPE reactor (6.5% *trans* and 23.8% $C_{18:0}$).

Results of the triacylglycerol (TAG) analysis indicated that the electrochemically hydrogenated soybean oils would have greater oxidative stability than the soybean oil starting material because of greater amounts of TAG with oleic acid and saturated fatty acids (Table 4). In addition, oil products hydrogenated to IV 92 at 80°C with a Pd catalyst cathode (see Table 3) would have the best oxidative stability and be a potential margarine or shortening basestock because of higher levels of PSS and SSS (S = stearate; P = palmitate). On the other hand, the IV 105 soybean oil processed at 50°C with a Pd cathode (Table 3) would be acceptable as a frying oil because of higher levels of OOO, POO, and LOS (O = oleate, L = linoleate).

Additional examples of SPE reactor performance, for canola and cottonseed oil feeds, are presented in Tables 5 and 6 for a reaction temperature of 60°C, a reactor pressure of 1 atm, and a constant current density of 0.1 A/cm^2. As was true for soybean oil, a Pd-black cathode performed best, in terms of fatty acid selectivities and oil hydrogenation CE, but the *trans* isomers content of the oil product was lower when a Pt-black cathode was employed in the SPE reactor.

For completeness during our preliminary evaluation of the SPE reactor, we also examined the partial hydrogenation of a two-component mixture of C_{18} fatty acid methyl esters that was prepared in our laboratory and an industrial-grade C_{18} fatty acid mixture. The results of these experiments with a Pt-black or Pd-black cathode are listed in Tables 7 and 8, where the current density was 0.10 A/cm^2, the reactor pressure was 1 atm, and the reaction temperature was either 70°C for the fatty acid starting material or 60°C for the fatty acid methyl ester mixture. The high-pressure and -temperature chemical catalytic hydrogenation of fatty acids is a more difficult reaction to carry out than the hydrogenation of edible oils, owing in part to the presence of impurities in industrial fatty acid process streams (such as fatty acid streams from deodorization distillates). This was also true for electrochemical fatty acid hydrogenations in an SPE reactor, as evidenced by the low hydrogenation CE in Table 7. Once again, we found that a Pd-catalyst cathode worked better than Pt in the SPE reac-

TABLE 6
SPE Reactor Performance and Chemical Properties of Electrohydrogenated Cotton Seed Oil[a]

	Fatty acid profile (area %)					%		Voltage	CE
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	IV	Trans	SLo	drop (V)	(%)
Starting oil	2.4	18.1	55.4	0.0	112	0			
Pt cathode	9.6	20.3	46.2	0.0	98	0.8	0.50	1.7	20.9
Pd cathode	10.7	27.3	38.5	0.0	90	4.3	1.11	1.65	47.8

[a]RuO_2 anode, 60°C reactor temperature, 1 atm. reactor pressure, 0.10 A/cm^2 current density. See Table 1 for abbreviations.

TABLE 7
SPE Reactor Performance for the Electrohydrogenation of a Fatty Acid Mixture[a]

	Fatty acid profile (area %)				IV	Voltage drop (V)	CE (%)
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$			
Starting fatty acids	13.2	44.9	35.8	2.2	106.4		
Pt cathode	14.0	46.8	36.2	0.7	104.8	1.6→3.5	3.3
Pd cathode	20.1	52.0	23.2	0.6	86.5	1.6→2.2	27.0

[a]RuO_2 anode, 70°C reactor temperature, 1 atm reactor pressure, 0.10 A/cm^2 current density. See Table 1 for abbreviations.

TABLE 8
SPE Reactor Performance for the Electrohydrogenation of a Fatty Acid Methyl Ester Mixture[a]

	Fatty acid profile (area %)				IV[b]	Voltage drop (V)	CE (%)
	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$			
Initial fatty acid methyl esters	0.0	70.9	29.0	0.0	111		
Pt cathode	15.7	66.0	18.1	0.0	88	1.6→1.9	34.5
Pd cathode	11.2	74.3	14.4	0.0	89	1.65	50.3

[a]RuO_2 anode, 70°C reactor temperature, 1 atm. reactor pressure, 0.10 A/cm^2 current density.
[b]See Table 1 for abbreviations.

tor, in terms of the hydrogenation CE and the anode/cathode voltage drop. The precise cause of the unusually high voltage drop of 3.5 V for the Pt-black cathode has not been identified but was probably due to catalyst poisoning. Significantly higher CE values were obtained when the fatty acid mixture was replaced by two purified fatty acid methyl esters (*cf.* Table 8). For the same product IV, less $C_{18:0}$ methyl ester was formed when the hydrogenation reaction was carried out at a Pd cathode (this result is consistent with the higher selectivities observed with a Pd cathode).

ACKNOWLEDGMENTS

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