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ORIGINAL PAPER

Production of Low-*trans* Fatty Acids Edible Oil by Electrochemical Hydrogenation in a Diaphragm Reactor Under Controlled Conditions

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Abstract Electrochemical hydrogenation is a novel, alternative process for selective hydrogenation of vegetable oils, because of its high extent of hydrogenation and low *trans*-isomer formation. Electrochemical hydrogenation of soybean oil in a diaphragm reactor with a formate ion concentration of 0.4 mol/l at pH 5.0 under moderate temperature conditions using a current density of 10 mA/cm^2 was investigated to identify the critical conditions affecting the selective hydrogenation reaction and the resulting fatty acid profile. The optimum composition was an oil-to-formate solution ratio of 0.3 (*w*/*w*), 2–3 g EDDAB in 100 g soybean oil, and 0.8% Pd–C catalyst loading. The electrochemical hydrogenation reaction of soybean oil was described by first-order kinetics, and the kinetic rate constants and reaction selectivity were determined accordingly. Re-use of the Pd–C catalyst up to five times was found to be acceptable. A comprehensive evaluation revealed that the most significant conditions affecting the extent of hydrogenation and the *trans* fatty acids content of final products were operating temperature, pH of the formate solution, and catalyst loading.

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Introduction

Clinical and epidemiological studies both provide evidence that *trans* fatty acid (TFA) intake increases the risk of heart disease and cancer [1–3]. TFAs are found naturally, at low levels, in meat and dairy products as a result of microbial hydrogenation of *cis*-unsaturated fatty acids in the stomach of ruminant animals. However, the major sources of TFAs are products containing industrially produced partially hydrogenated vegetable oils used as alternatives to lard and butter in processed food [4]. Increasing concerns about the consumption of TFAs have led consumers to demand reform of conventional edible oil hydrogenation technology, accompanied by vast movements to require manufacturers to label *trans* fats in food products, strict regulation of the sale of foods containing TFAs, and possible banning of TFAs [5]. Recently, a number of techniques have been developed and are currently in use by the food and edible oil industries to produce products with minimal to zero TFA. Compared with other types of catalytic hydrogenation, electrochemical hydrogenation is regarded as a more efficient modification of the gas hydrogenation process. Electrochemical hydrogenation of oils at low operating temperatures (<70 °C) has been extensively investigated, and TFAs can be reduced to less than 10% of the oil content while increasing selectivity for unsaturated fatty acids [6–8].

In existing electrolytic approaches, some setups have been reported in the literature as pathways capable of transferring the hydrogen donors via various routes. For example, a process was established in which the hydrogen donors could be transferred through a proton-exchange membrane (PEM) with the source of protons derived from the electrolytic water at the anode [6, 9]. Another mediator-assisted system, which employs electrolytes such as sodium formate and formic acid, was reported to effectively carry protons to the double bonds of unsaturated fatty acids [7]. However, it was not until recently that our research team successfully demonstrated a novel electrochemical hydrogenation system using a diaphragm reactor [8]. In this reactor, the regeneration of formate ion as the shuttle can occur directly at the cathode area in situ, whereas the hydrogen proton donors transfer through the PEM from anode to cathode, thus resulting in reduced addition of formic acid and lower acid value of products than that of the mediator-assisted system [7]. Specifically, during the hydrogenation of soybean oil, the diaphragm reactor was able to operate successfully for 6 h, furnishing a hydrogenated oil with 8.62% TFAs and an iodine value (IV) of 88.86 g I_2/100 g oil. With the catalyst Pd–C, conditions resulting in a low specific isomerization index were achieved using 0.4 mol/l formate ion at pH 5.0 and 60 °C and a constant applied current density of 10 mA/cm^2 [8].

Theoretically, the extent of electrochemical hydrogenation and the selectivity of fatty acid reactions are both highly dependent not only on the aforementioned operating conditions (e.g. temperature, pH, current density, and agitation speed), but also on the composition of substances involved in the reaction. Moreover, there have been limited reports concerning the effect of multi-phase mixture compositions, which are also crucial in determining the performance of the hydrogenation process. In order to further increase selectivity for linolenic acid, reduce the formation of TFAs, and improve the efficacy of this new approach, the objectives of this study were to characterize the effects of a range of conditions critical to electrochemical hydrogenation, including oil-to-formate solution ratio (OFR), emulsifier concentration, catalyst loading, and activation energy of the reaction, and the effect of using recycled Pd–C catalyst on fatty acid profiles, IV, TFA content, and hydrogenation selectivity. A comprehensive evaluation for optimization was also conducted to assess the significance of the variables investigated with regard to scale-up of the electrochemical hydrogenation operation.

Materials and Methods

Electrochemical Hydrogenation

Oil hydrogenation was carried out in a batch diaphragm electrochemical reactor made of iridium–titanium (Ir–Ti) alloy [8]. A Nafion 117 cation-exchange membrane (E.I. Dupont de Nemours, Wilmington, DE, USA) was inserted and bolt-secured between the cathode and anode chambers. In addition, grids of ruthenium–iridium (Ru–Ir) alloy coated with zirconium–titanium (Zr–Ti) were fixed on the opposite surfaces of the membrane to protect the Nafion membrane from shear force generated by the electrolytic solvents. Equilibration of the reactions was achieved by submerging the sealed reactor in a temperature-controlled water bath. The anode and cathode, both comprising platinum mesh with surface areas of 2.2 and 1 cm^2, respectively, were connected to a digital coulometer (model 640, The Electrosynthesis Company, Amherst, NY, USA) to monitor the total electrical charge within the circuit during the experiment. An electric blender was used to agitate the oil–water mixture in the cathode region to provide sufficient dispersion of the oil and catalyst powder in an aqueous solution of formate. A G 750 potentiostat (Gamry Instrument, Warminster, PA, USA) equipped with a data-acquisition system was used as the source of electrical current.

Pd–C powder catalyst suspended in an oil-formate solution under agitation was used in the hydrogenation reaction. To initiate the reactions, dodecyldimethylethyl ammonium bromide (EDDAB) (Xuanguang, Nanjin, China) was added to the cathode chamber containing a mixture of total volume 70 ml of refined and deodorized soybean oil (Northsea oil and Grains, Tianjin, China) and formate solution (Sigma–Aldrich, St Louis, MO, USA). Then 70 ml 0.05 M sulfuric acid (Sigma–Aldrich) was added to the anode chamber. The mixture was stirred and heated to the specified temperature in the water bath, followed by the addition of 5% (*w*/*w*) Pd–C catalyst with a surface area of 900 m^2/g (Dalian Toyounger Chemical, Dalian, China) to the cathode chamber. Unless otherwise mentioned, a typical electrochemical oil hydrogenation took 6 h with an applied electrical current density of 10 mA/cm^2, a formate concentration of 0.4 M, and formate solution of pH 5.0.

Recovery of Oil Products and Pd–C Catalyst

On completion of the reaction, a sample containing the oil phase (which included the catalyst) was diluted with *n*-hexane and a saturated NaCl (ca. 5 ml) solution, adequately vortex mixed, and centrifuged (1,000×*g*) for 5 min to separate it from the aqueous phase. After isolation of the catalyst by filtration, the supernatant containing the *n*-hexane and oil was pipetted into test tubes, then vacuum-evaporated to remove the *n*-hexane. The residual oil sample was collected to determine the fatty acid composition [8]. In order to make the catalyst reusable, the solid particles of Pd–C catalyst were collected and submersed in 20% NaOH solution for 4 h at room temperature with continuous slow agitation, to ensure most of the formate ions on the surface of the catalyst dissolved in the alkaline solution. The catalyst was then separated by filtration and rinsed three times with deionized water until the residual solution attained a pH of 7.0. The catalyst was then added to a 5% NaOH solution and treated under the same conditions to ensure removal of any remaining soap and emulsifier adsorbed on the surface of the catalyst. After rinsing with deionized water, the Pd–C catalyst particles were collected and dried at 120 °C for 4 h for recovery [10].

Determination of Fatty Acid Composition

Methyl esters were prepared according to the official method AOCS Ce 2-66 [11] for determination of total TFA content and the composition of fatty acids. Fatty acid composition was determined using a 6890N Network GC System gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a flame-ionization detector and a cold on-column injector [8]. An HP-88 capillary column (100 m × 0.25 mm i.d.) coated with cyanopropylpolysiloxane (film thickness 0.2 μm) (PN112-88A7, Agilent Technologies) was used. Hydrogen (purity >99.9997%) was used as the carrier gas and maintained at a constant flow rate of 0.8 ml/min. The temperatures of the injector and the flame ionization detector were set at 240 and 250 °C, respectively. The oven was held at an initial temperature of 180 °C for 110 min, then increased at a rate of 30 °C/min to a final temperature of 210 °C, which was held for 3 min. The inlet split ratio was 100:1. Heptadecanoic methyl ester ($C_{17:0,}$ Sigma–Aldrich) was used as an internal standard. The injection volume of each sample was 1 μl. Analyses were conducted in duplicate and the mean results for each sample are reported. Twenty individual fatty acid methyl esters standards, including $C_{8:0}$, $C_{10:0}$, $C_{12:0}$, $C_{14:0}$, $C_{16:0}$, $C_{16:1}$ t-9, $C_{16:1}$ c-9, $C_{18:0}$, $C_{18:1}$ t-9, $C_{18:1}$ c-9, $C_{18:1}$ t-11, $C_{18:2}$ t-9,12, $C_{18:2}$ c-9,12, $C_{18:3}$ t-9,12,15, $C_{18:3}$ c-6,9,12, $C_{18:3}$ c-9,12,15, $C_{20:0}$, $C_{22:0}$, $C_{22:1}$ c-13, and $C_{24:0}$, were used (Sigma–Aldrich). The results are expressed in g/100 g total fatty acid.

The total TFA content of foods was determined using Fourier transform infrared (FTIR) spectroscopy (AOCS Cd 14-95). A Nicolet Avatar 370 Infrared Spectrometer (Nicolet Instrument, Madison, WI, USA) was used. FTIR spectra between 900 and 1,050 cm^{-1} were captured and the absorption band at 966 cm^{-1} was measured; a standard curve was established by using methyl elaidate ($C_{18:1}$ t-9) standards (Sigma–Aldrich). All samples were equilibrated at 24 °C, and three replicates were conducted for each sample.

Characterization of Hydrogenated Soybean Oil

The hydrogenated soybean oil samples produced using the aforementioned apparatus were analyzed to determine IV and acid value in accordance with AOCS methods Cd 1c-85 and 5a-40, respectively. As determined from the initial and final fatty acid triene and diene profiles of the soybean oil samples and from first-order rate kinetics for fatty acid hydrogenation, the hydrogenation selectivities of linolenic acid (SLn) and linoleic acid (SLo) were computed from the rate constant ratios K_1/K_2 and K_2/K_3, respectively [8, 12]. The specific *trans* isomerization index (SII), which is defined as the percentage increase in TFA content per unit change in the oil's IV, was also determined [12]. Analyses were conducted in triplicate, and the mean results from each of the samples are reported.

Statistical Analysis

To determine the effects of the conditions used for hydrogenation, experiments were performed in triplicate and mean values are reported. Data were analyzed using SPSS for Windows (Version Rel. 10.0.5, 1999; SPSS, Chicago, IL, USA). Between-group differences were calculated using one-way ANOVA for repeated measures, followed by Tukey's post-hoc test using the experimental data points. Significance data from post-hoc analysis are reported.

Results and Discussion

Effect of Oil-to-Formate Solution Ratio

The effect of OFRs ranging from 0.1 to 0.4 (*w*/*w*) on the extent of hydrogenation and on the fatty acid profile was characterized (Fig. 1). IV declined sharply as OFR was increased from 0.1 to 0.3, SLn remained nearly constant and SLo increased (Table 1), suggesting that the rate of hydrogenation of dienes was promoted, and with elevated levels of hydrogenation. However, further increases in the amount of oil (OFR >0.3) were found to result in a slight

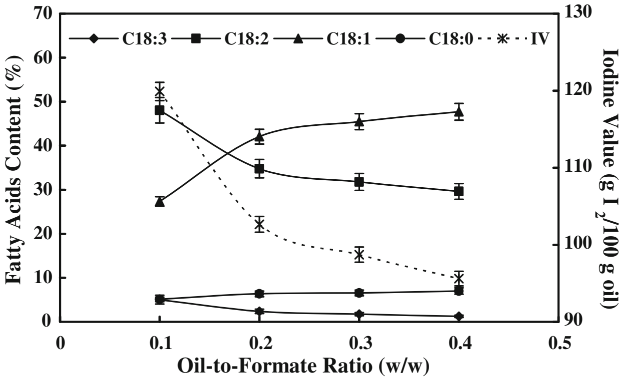

Fig. 1 Effect of oil-to-formate solution ratio on hydrogenation of soybean oil (0.4 M formate, 0.3 g Pd/100 g oil, 0.02 g EDDAB/g oil, pH 5.0, 60 °C, current density 10 mA/cm^2, 6 h, and 650 rpm)

Table 1 Effect of oil-to-formate solution ratio (OFR) on *trans* fatty acids content (TFAs), specific isomerization index (SII), and hydrogenation selectivity SLn and SLo

Oil-to-water ratio (*w*/*w*)	TFAs[a] (% fat, *w*/*w*)	SII	SLn	SLo
0.1	3.5a ± 0.1	0.24a ± 0.02	2.33c ± 0.07	4.84a ± 0.09
0.2	8.0b ± 0.2	0.25a ± 0.01	2.05a ± 0.01	8.91b ± 0.07
0.3	10.7c ± 0.1	0.31b ± 0.03	2.18b ± 0.04	10.07c ± 0.05
0.4	12.5c ± 0.2	0.33b ± 0.04	2.38c ± 0.01	9.96c ± 0.04

Experimental conditions were 0.4 M formate, 0.3 g Pd/100 g oil, 0.02 g EDDAB/g oil, pH 5.0, 60 °C, current density 10 mA/cm^2, reaction time 6 h, and 650 rpm

[a] Data are expressed as mean ± SD ($n = 3$). Values in the same column followed by different letters are significantly different ($P < 0.05$)

decrease in the IV (ca. 4%). Meanwhile, it is clear that the SII increased with the increasing OFR. Such OFR dependency and degree of hydrogenation could possibly be attributed to the equilibrium of the reaction of substances in electrochemical hydrogenation.

In the cathode chamber of the electrochemical reactor, the major electrochemical reaction between the unsaturated fatty acids of the oil and the formate ions, in the presence of Pd as hydrogenation catalyst and EDDAB as emulsifier, is shown in reaction 1 [8, 13]:

$$\mathrm{HCOO^- + H_2O + Oil \xrightarrow{Pd} Oil - H_2 + HCO_3^-}. \quad (1)$$

From the chemical equilibrium standpoint, 1 mol soybean oil should react with 1 mol formate ion. This means that soybean oil triglyceride molecules, with an average size of 1,100 Da (in what is regarded as one of the most well-balanced oils with above 80% fatty acids with 18 carbon bonds) should react with formate ions of 45 Da in order to complete the hydrogenation reaction. For instance, when adding hydrogen to 20 g soybean oil, approximately 50 g 0.4 M formate solution should be adequate for the reaction. This could explain why the IV value decreased rapidly and high SLo was achieved at a relatively low OFR of 0.3. This result was in agreement with a similar observation of oil-to-water ratio conducted in a different reactor [7]. In contrast, under higher OFR (>0.3, *w*/*w*) conditions, the rate of hydrogenation was found to be much less than that for lower OFR, because of the presence of excess oil which was not hydrogenated, as manifested by the increased TFA content (Table 1). In fact, not only will use of redundant substrates be cost-prohibitive, the resulting oil or formate solution will also hinder the effectiveness of downstream recovery and purification processes. Therefore, it is advisable that a reasonable OFR of 0.3 (*w*/*w*) should be chosen for practical applications.

Effect of Emulsifier Loading

EDDAB as an emulsifier was added to minimize the surface tension caused by the interface layers of the three phases in the cathode chamber, namely refined soybean oil, formate solution, and catalyst powder. The effect of emulsifier loading on the reaction process was investigated in terms of IV and the composition of the hydrogenated oil (Fig. 2). Compared with the original oil, which had an IV of 130.04 g I_2/100 g oil, there was negligible hydrogenation (2%) in the absence of an emulsifier. When EDDAB was added at a level of 2 g/100 g oil, an obvious decrease of IV (ca. 20%) was observed accompanied by simultaneous decreases in linolenate ($C_{18:3}$) and linoleate ($C_{18:2}$) levels. Although the degree of hydrogenation stayed relatively flat with increased loading of EDDAB above 2 g/100 g oil, it should be noted that SII still decreased slightly, (Table 2), suggesting that the presence of excess emulsifier could effectively improve the adsorption stability of hydrogen donors in the active sites of interface layers among reagents—oil, mediator solution, and catalyst. Based on these data, it can be concluded that addition of 2–3 g EDDAB to 100 g soybean oil is reasonable.

Effect of Catalyst Loading and Recycling of the Pd–C Catalyst

Pd–C powder catalyst was used in the hydrogenation reaction, because of its unique catalytic activity, namely

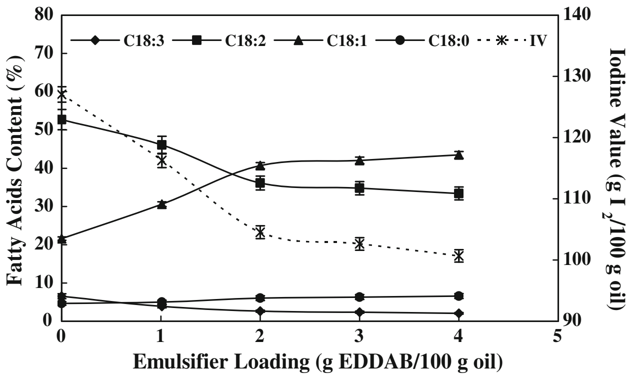

Fig. 2 Effect of emulsifier loading on hydrogenation of soybean oil (0.4 M formate, 0.3 g Pd/100 g oil, 0.2 g oil/g formate solution, pH 5.0, 60 °C, current density 10 mA/cm^2, 6 h, and 650 rpm)

Table 2 Effect of emulsifier loading on *trans* fatty acids content (TFAs), specific isomerization index (SII), and hydrogenation selectivity SLn and SLo

Emulsifier loading (g EDDAB/100 g oil)	TFAs[a] (% fat, *w*/*w*)	SII	SLn	SLo
0	2.5a ± 0.1	0.45c ± 0.04	2.85d ± 0.07	2.76a ± 0.08
1.0	5.2b ± 0.2	0.30b ± 0.02	2.77c ± 0.01	8.86b ± 0.04
2.0	7.7c ± 0.2	0.26a ± 0.01	2.02a ± 0.01	9.10c ± 0.10
3.0	8.0c ± 0.2	0.25a ± 0.01	2.05a ± 0.01	8.91b ± 0.07
4.0	8.1c ± 0.1	0.24a ± 0.01	2.13b ± 0.03	8.80b ± 0.05

Experimental conditions were 0.4 M formate, 0.3 g Pd/100 g oil, 0.2 g oil/g formate solution, pH 5.0, 60 °C, current density 10 mA/cm^2, reaction time 6 h, and 650 rpm

[a] Data are expressed as mean ± SD ($n = 3$). Values in the same column followed by different letters are significantly different ($P < 0.05$)

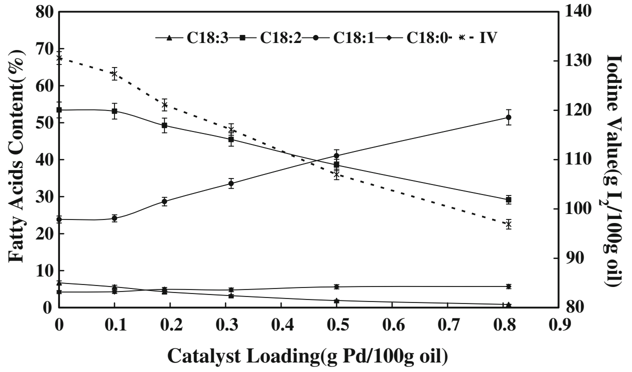

Fig. 3 Effect of catalyst loading on hydrogenation of soybean oil (0.4 M formate, 0.02 g EDDAB/g oil, 0.2 g oil/g formate solution, pH 5.0, 60 °C, current density 10 mA/cm^2, 6 h, and 650 rpm)

production of less geometrical and positional isomers at a rate 30–100 times greater than by nickel and other commercially available hydrogenation catalysts [14, 15]. Furthermore, our experiments showed that Pd–C was a more effective catalyst than the well-known Raney nickel catalyst in this system, which could possibly be attributed to the higher activity of Pd catalysts over Ni under milder conditions [16]. This result corresponded well with findings in a catalytic transfer hydrogenation of soybean oil using formic acid salts as donors [17]. As seen in Fig. 3, a significant decrease in the IV was observed when the catalyst loading was increased from 0.1 to 0.8% (Pd in oil, *w*/*w*), whereas production of TFAs increased with increasing catalyst loading, resulting in the SII remaining fairly constant for catalyst loading above 0.2% (Table 3). Such phenomena could be attributed to the sufficient active sites made available by addition of the catalyst, and subsequent reduction of the rate of desorption of hydrogen atoms on the catalyst surface. Therefore, a highly hydrogenated oil containing a low-level of *trans* isomers could be produced.

To date, insufficient information is available in the literature on the recycling of Pd–C catalyst in electrochemical hydrogenation of oil, although it was notable that Pd–C had good recycle properties in formate transfer hydrogenation [17]. With the diaphragm setup used in this study (Fig. 4), Pd–C catalyst could be repeatedly used up to five times with negligible change in the IV of the finished oil products. When Pd–C catalyst was used for the sixth time, the extent of hydrogenation was decreased slightly, as indicated by the increase in IV (ca. 10%). Theoretically, the chemical catalyst should be recoverable and reusable indefinitely after use, because it is not consumed in the chemical reactions. However, it is well recognized that catalysts cannot be used endlessly mainly because of poisoning and particle compaction that occur when subjected to prolonged heating and sequential corrosion in alkaline or acidic solutions [17]. Therefore, it can be postulated that loss of catalytic activity occurred over time in the presence of the weakly acidic formate electrolytes of pH 5.0, even at a relatively moderate operating temperature (<70 °C).

Activation Energy of Electrochemical Hydrogenation

During electrochemical hydrogenation, unsaturated fatty acids compete with hydrogen donors by adsorption on the active sites on the catalyst surface where they are gradually converted to a saturated state. With regard to the complexity of hydrogenation, which involves a series of saturation and isomerization reactions of unsaturated fatty acids, a first-order and irreversible reaction model was commonly accepted as determining the kinetic rate constants of hydrogenation. Moreover, from the results of previous research, the first-order kinetics mechanism was in satisfactory agreement with the experimental data under various operating conditions [17–20]. Generally, the rate constants have an Arrhenius relationship with temperature, in accordance with Eq. 2:

$$\mathrm{Ln}\ k = \mathrm{Ln}\ k_0 - \frac{E}{RT}. \tag{2}$$

Table 3 Effect of catalyst loading on the *trans* fatty acids content (TFAs), specific isomerization index (SII), and hydrogenation selectivity SLn and SLo

Catalyst loading (g Pd/100 g oil)	TFAs[a] (% fat, *w/w*)	SII	SLn	SLo
0.1	3.7a ± 0.2	0.19a ± 0.03	6.56d ± 0.06	0.57a ± 0.06
0.2	6.5b ± 0.1	0.36b ± 0.01	3.48c ± 0.03	1.89b ± 0.12
0.3	8.6c ± 0.1	0.38b ± 0.03	3.12b ± 0.03	3.89c ± 0.01
0.5	12.3d ± 0.1	0.39b ± 0.03	2.92a ± 0.03	5.71d ± 0.06
0.8	15.3e ± 0.3	0.36b ± 0.05	2.81a ± 0.05	11.32e ± 0.07

Experimental conditions were 0.4 M formate, 0.02 g EDDAB/g oil, 0.2 g oil/g formate solution, pH 5.0, 60 °C, current density 10 mA/cm^2, reaction time 6 h, and 650 rpm

[a] Data are expressed as mean ± SD ($n = 3$). Values in the same column followed by different letters are significantly different ($P < 0.05$)

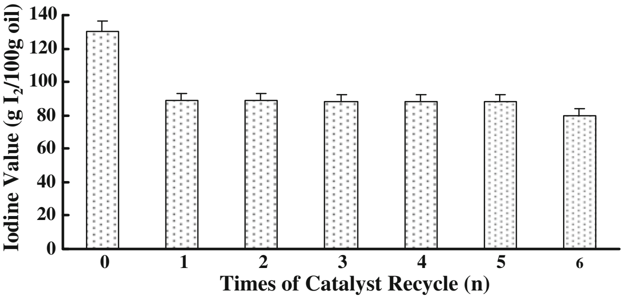

Fig. 4 Effect of recycle times of Pd–C catalyst on hydrogenation of soybean oil (0.4 M formate, 0.02 g EDDAB/g oil, 0.2 g oil/g formate solution, 0.8 g Pd/100 g oil, pH 5.0, 60 °C, current density 10 mA/cm^2, 6 h, and 820 rpm)

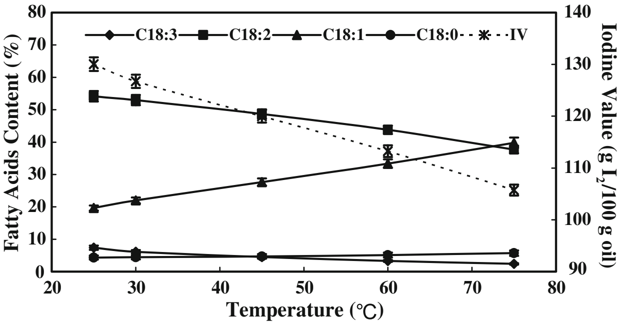

Fig. 5 Effect of temperature on hydrogenation of soybean oil (0.4 M formate, 0.02 g EDDAB/g oil, 0.2 g oil/g formate solution, 0.2 g Pd/100 g oil, pH 5.0, current density 10 mA/cm^2, 6 h, and 650 rpm)

Table 4 Effect of temperature on rate constants of electrochemical hydrogenation

T (°C)	$K_1 \times 10^3$ (h^{-1})[a]	$K_2 \times 10^3$ (h^{-1})	$K_3 \times 10^3$ (h^{-1})
30	20.5a ± 0.5	5.0a ± 0.3	0.6a ± 0.1
45	54.3b ± 0.7	18.0b ± 0.7	1.6b ± 0.2
60	88.5c ± 0.5	32.7c ± 0.5	3.1c ± 0.1
75	125.8d ± 0.2	52.2d ± 0.8	4.9d ± 0.3

Experimental conditions were 0.4 M formate, 0.02 g EDDAB/g oil, 0.2 g oil/g formate solution, 0.2 g Pd/100 g oil, pH 5.0, current density 10 mA/cm^2, reaction time 6 h, and 650 rpm

[a] Data are expressed as mean ± SD (n=3). Values in the same column followed by different letters are significantly different ($P < 0.05$)

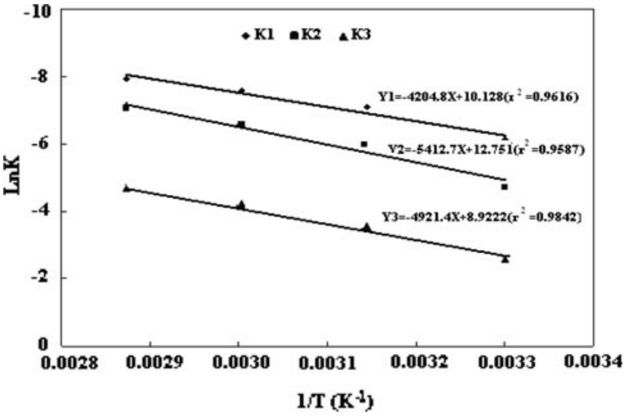

Fig. 6 Effect of temperature on rate constants of hydrogenation of soybean oil (0.4 M formate, 0.02 g EDDAB/g oil, 0.2 g oil/g formate solution, 0.2 g Pd/100 g oil, pH 5.0, current density 10 mA/cm^2, 6 h, and 650 rpm

By application of the Arrhenius equation to results from determination of the effect of temperature on the hydrogenation (Fig. 5), the values of the appropriate Arrhenius constants, namely the pre-exponential factor K_0 and the activation energy E, were obtained, incorporating the calculated rate constants K_1, K_2, and K_3 under the conditions 30, 45, 60, and 75 °C (Table 4). Experimentally, the rate constants obtained from the kinetic model showed that the rate of hydrogenation of oleic acid is much slower than that of linolenic and linoleic acids. From the temperature dependence of the various stage reaction rate constants, the activation energy of trienes, dienes, and monoenes were found to be 34.96, 45.00, and 40.92 kJ/mol, respectively

Table 5 Pre-exponential factor K_0 and activation energy E of electrochemical hydrogenation

Fatty acid profiles	K_0 (mol%$^{-1}$ h^{-1})	E (kJ/mol)
Trienes	2.50×10^4	34.96
Dienes	3.45×10^5	45.00
Monoenes	7.50×10^3	40.92

Experimental conditions were 0.4 M formate, 0.02 g EDDAB/g oil, 0.2 g oil/g formate solution, 0.2 g Pd/100 g oil, pH 5.0, current density 10 mA/cm^2, reaction time 6 h, and 650 rpm

(Table 5). Moreover, the set of plots of Ln K versus 1/T gives the activation energy and pre-exponential factor for electrochemical hydrogenation; the lines of K_1, K_2, and K_3 obtained at different temperatures, with correlation coefficients, are shown in Fig. 6. These data clearly indicate that the reaction is kinetically controlled under the conditions used for hydrogenation, and electrochemical hydrogenation of soybean oil with Pd–C (5%, *w*/*w*) catalyst accords well with a pseudo-first-order kinetic model. These values are a reasonable match with those reported in studies using sodium formate as donor [20]. Furthermore, because the reaction activation energy determines the sensitivity of the catalyst to temperature increases and hence reduces the difficulty of thermal reaction, lower values of activation energy were achieved in this setup compared with the similar reaction of soybean oil using ammonium formate as the donor in catalytic transfer hydrogenation [21], suggesting that the Pd–C catalyst led to better performance with use of formate electrolytes, which in turn resulted in reduced *trans* isomer generation in electrochemical hydrogenation.

Mathematical Model for Electrochemical Hydrogenation

To analyze the effect of the conditions used in electrochemical hydrogenation, a stepwise approach to the defined optimum was used, using the quadratic factorial model. With formate solution as hydrogen donor and electrochemically oxidized protons, the hydrogenation process is dependent on five key processing conditions—temperature, the pH of formate solution, catalyst loading, emulsifier loading, and OFR. Based on the design of 2^4 factorial models (Table 6), their effects on IV and TFAs content could be assessed using 1–16 factorial experiments. As seen in Tables 7 and 8, the significance of the linear and cross-product effect of each condition on IV and TFAs was identified individually. Analysis of variance furnished F values for temperature, pH of the formate solution, and catalyst loading indicative of highly significant effects on IV and TFAs of the final products. In addition, OFR and the cross-product between emulsifier loading and OFR also had significant effects on IV, suggesting that the degree of hydrogenation was very complex, and the relationship for each factor did not follow a simple linear function, but rather a quadratic function. Moreover, both models of "$Pr > F$" less than 0.05 implied that the model equations were adequate, and could be used to simulate the real experimental data.

Conclusion

Electrochemical hydrogenation in a diaphragm electrochemical reactor using formate ions as the mediator and

Table 6 Factorial experimental design for optimization of electrochemical hydrogenation using the quadratic model

Trial	Temperature (°C)	pH	Catalyst loading (g Pd/100 g oil)	Emulsifier loading (g EDDAB/100 g oil)	OFR (*w*/*w*)	IV (g I_2/100 g oil)	TFAs (%)
1	55	4.5	0.8	2.5	0.3	96.6	12.08
2	55	4.5	0.8	3.5	0.2	96.4	10.72
3	55	4.5	1.2	2.5	0.2	95.3	12.93
4	55	4.5	1.2	3.5	0.3	93.4	13.21
5	55	5.5	0.8	2.5	0.2	107.7	9.91
6	55	5.5	0.8	3.5	0.3	101.7	9.64
7	55	5.5	1.2	2.5	0.3	96.3	10.98
8	55	5.5	1.2	3.5	0.2	100.0	13.12
9	65	4.5	0.8	2.5	0.2	93.1	17.57
10	65	4.5	0.8	3.5	0.3	91.9	16.10
11	65	4.5	1.2	2.5	0.3	81.3	23.60
12	65	4.5	1.2	3.5	0.2	88.6	18.43
13	65	5.5	0.8	2.5	0.3	93.2	13.45
14	65	5.5	0.8	3.5	0.2	92.5	13.56
15	65	5.5	1.2	2.5	0.2	92.2	17.23
16	65	5.5	1.2	3.5	0.3	92.0	16.12

Experimental conditions were 0.4 M formate, current density 10 mA/cm^2, reaction time 6 h, and 650 rpm

Table 7 Analysis of variance for the iodine value after electrochemical hydrogenation

Source	df[a]	IV of soybean oil products (g I_2/100 g oil)				
		Sum of squares	Mean squares	*F* value	*Pr* > *F*	Significance
Model[b]	6	467.16	77.86	18.80	0.0001	
Residual	9	37.28	4.14			
Cor total	15	504.44				
A—temperature	1	244.93	244.93	59.13	<0.0001	**
B—pH	1	95.06	95.06	22.95	0.0010	**
C—catalyst loading	1	72.25	72.25	17.44	0.0024	**
D—emulsifier loading	1	0.04	0.04	0.01	0.9239	
E—OFR	1	23.52	23.52	5.68	0.0410	*
DE	1	31.36	31.36	7.57	0.0224	*

[a] *df* degrees of freedom

[b] Model equation $IV = 175.48 - 0.78A + 4.88B - 10.63C - 13.90D - 192.25E + 56.00DE$

* Significance at the 0.05 level

** High significance at the 0.01 level

Table 8 Analysis of variance for *trans*-isomer content after electrochemical hydrogenation

Source	df[a]	*trans*-isomer content of soybean oil products (%)				
		Sum of squares	Mean squares	*F* value	*Pr* > *F*	Significance
Model[b]	6	179.71	35.94	11.05	0.0003	
Residual	9	25.15	2.51			
Cor total	15	204.86				
A—Temperature	1	118.10	118.10	46.97	<0.0001	**
B—pH	1	26.60	26.60	10.58	0.0087	**
C—catalyst loading	1	31.89	31.89	12.68	0.0052	**
D—emulsifier loading	1	2.93	2.93	1.17	0.3055	
E—OFR	1	0.18	0.18	0.07	0.7930	

[a] *df* degrees of freedom

[b] Model equation $TFAs = -10.44 + 0.54A - 2.58B + 7.06C - 0.86D + 2.14E$

** High significance at the 0.01 level

Pd–C as catalyst was found to enable highly effective production of hydrogenated soybean oil with low TFA at moderate processing temperature and atmospheric pressure. The critical composition of substrates in this multiphase mixture of hydrogenated oil was identified, namely OFR, emulsifier concentration, and catalyst loading, and the optimum values were found to be 0.3 (*w*/*w*), 2–3 g EDDAB in 100 g soybean oil, and 0.8% Pd–C catalyst loading, respectively. In addition, the activation energy of the reaction and the efficiency for recycling of the Pd–C catalyst up to five times were also investigated. A comprehensive evaluation showed that the significant conditions affecting the extent of hydrogenation were the operating temperature, the pH of the formate solution, and catalyst loading.

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