J Am Oil Chem Soc (2008) 85:1087–1096
DOI 10.1007/s11746-008-1294-y

ORIGINAL PAPER

# Production of Low Acid Value Edible Oil with Reduced TFAs by Electrochemical Hydrogenation in a Diaphragm Reactor

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Received: 14 May 2008 / Revised: 13 August 2008 / Accepted: 18 August 2008 / Published online: 7 September 2008

**Abstract** A new diaphragm electrochemical system was devised and tested for hydrogenation of soybean oil under moderate processing temperature and atmospheric pressure. With proper loading of the catalyst Pd-C, the reactor was operated successfully for 6 h and yielded hydrogenated soybean oil containing 8.62% TFAs with an IV of 88.86 g $I_2$/100 g oil and an AV of 0.7 mg KOH/g oil. The low AV (acid value) of the hydrogenated oil, indicative of the oxidization tendency of the oil, is highly desirable from the industrial application standpoint. The low specific isomerization index was reached with 0.4 mol/L of formate ions at pH 5.0 under 60 °C using a constant applied current density (10 mA/cm$^2$). The extent of hydrogenation was found to increase with increasing current density, formate ion concentration, reaction temperature, catalyst loading, and speed of agitation. It was characterized that the extent of hydrogenation under low pH (2.0–5.0) was controlled by the regeneration of formate ion, whereas under high pH (6.0–10.0) the hydrogenation was influenced strongly by the formate ion stability.

**Keywords** Electrochemical hydrogenation · Diaphragm · Formate ion regeneration · Acid value · *trans* Fatty acids · Catalyst Pd-C

## Introduction

Hydrogenation of the unsaturated fatty acids in edible oil has been a common practice in producing products that are oxidatively stable while converting liquid oils to semisolid plastic fats similar in texture to butter, lard, and tallow. Increased concerns on the consumption of *trans* fatty acids (TFAs) due to the adverse heath risks have led to consumer's demand for reforming the conventional edible oil hydrogenation technology [1]. This also resulted in regulatory actions that obligate manufacturers to label *trans* fats in food products [2, 3], strictly regulate the sale of foods containing TFAs [4], or take active steps towards the possible banning of TFAs [5]. The physiology relevance of dietary TFAs to immune system functions has been extensively investigated during the last two decades [6]. Strong evidence has shown dietary TFAs influence the lipid composition of biological fluids of human milk and serum, and are inversely correlated to birth weight for neonates [7]. In addition, dietary TFAs can reduce serum HDL-cholesterol and increase LDL-cholesterol [8, 9]. Recently, dietary TFAs were found to result in the prevalence of symptoms of asthma, allergic rhinoconjunctivitis, and atopic eczema in childhood [10].

Use of electrochemical hydrogenation instead of gas hydrogenation has been reported and developed for edible oil since 1992 [11]. Many studies have demonstrated that electrochemical hydrogenation offers an advantage of producing final product with *trans* isomer fatty acids at lower levels than gas hydrogenation and subsequently

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much less thermal degradation, which could significantly reduce the consumer's concerns [12, 13]. In the process of electrochemical hydrogenation, the charge carried by the electron is involved in the reactions of various hydrogen donors and solvents, and the hydrogen concentration on the catalyst surface can be partially controlled by the applied current. Since hydrogen is generated in situ directly over the catalytic surface, there is no need for enhancement of hydrogen transfer rate, thereby eliminating the requirements to operate at high temperature (up to 150–225 °C) and high pressure (10–60 psig) that are required by the traditional gas hydrogenation. Most importantly, the expected targets of reducing TFAs while increasing the selectivity of unsaturated fatty acid can be achieved [14].

To date, two different setups were reported in the literature as pathways capable of transferring the hydrogen donors. The hydrogen donors could be transferred via a proton exchange membrane (PEM) with the source of protons derived from the electrolytic water at the anode [13, 15]. Or, a mediator-assisted system that employs electrolytes such as sodium formate and formic acid could effectively carry protons to the double bonds of unsaturated fatty acids. It has been well documented that both systems could produce products with significantly less *trans* isomers content under controlled conditions [14].

In the present study, a novel electrochemical hydrogenation system was developed. The regeneration of formate ions as the shuttle can occur in situ directly at the cathode area, whereas hydrogen proton donors are transferred through the proton exchange membrane from anode to cathode, resulting in less addition of formic acid than that of the mediator-assisted system developed by Mondal and Lalyani [14] .The acid value of products was investigated, focusing on the influence of the lower concentration of formic acid offered by the new approach. Moreover, the effects of a spectrum of parameters, including pH, temperature, speed of agitation, catalyst loading, and formate ion concentration on the fatty acids profiles, iodine value, *trans* fatty acids content, and hydrogenation selectivity were characterized.

## Materials and Methods

### Electrochemical Reactor Design

The oil hydrogenation was carried out in a diaphragm electrochemical reactor made of iridium-titanium (Ir-Ti) alloy. Compared with other metal reactors, Ir-Ti is regarded as an excellent alloy that offers a strong resistance to high operating temperature, corrosive solvents, and strain.

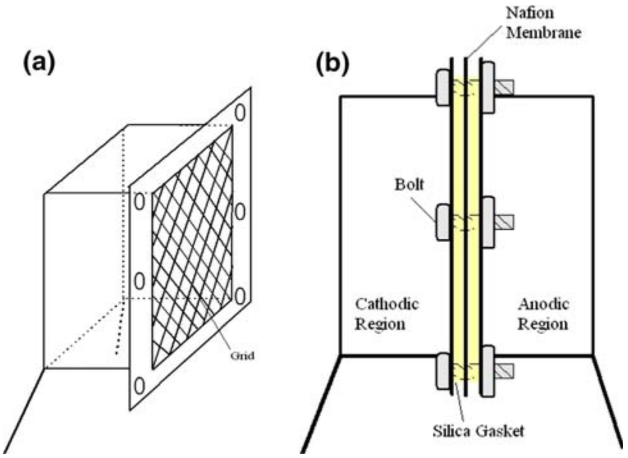

**Fig. 1** The configuration of diaphragm electrochemical hydrogenation reactor **a** chamber of a half of electrochemical hydrogenation reactor **b** schematic side cross-section of the diaphragm reactor

The configuration of half of the reactor (the cathode or anode chamber) with dimensions of 40 mm (length) × 30 mm (width) × 75 mm (height) is shown in Fig. 1a. A Nafion 117 cation exchange membrane (E. I. Dupont de NEMOURS, Inc., Wilmington, DE, USA) of 175 µm dry thickness was inserted and bolt-secured between the cathode and anode chambers (Fig. 1b). Widely used in membrane-electrode-assembly of $H_2/O_2$ fuel cells, a Nafion membrane permits proton migration through it under a constant applied electric field during reactor operation [16]. The grids of ruthenium-iridium (Ru-Ir) alloy coated with zirconium-titanium (Zr-Ti) were then fixed on the opposite surfaces of the membrane to protect the Nafion membrane from the shear force generated by the electrolytic solvents. The grids were surrounded by silica gaskets (1-mm thickness) and properly secured with stainless steel bolts to ensure that both chambers were well connected and the reactor sealed.

The thermostat of the reactions was achieved by submerging the sealed reactor into a temperature-controlled

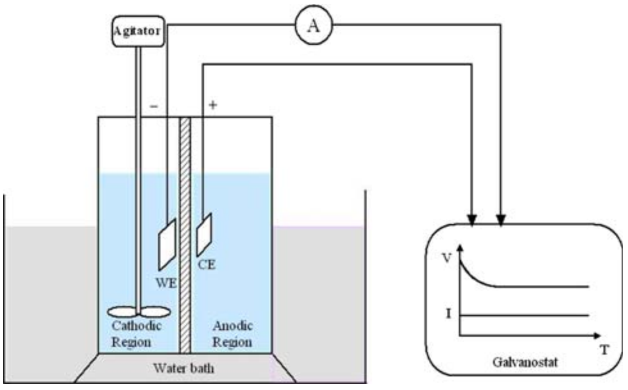

**Fig. 2** Laboratory scale mode setup of diaphragm electrochemical hydrogenation

water bath (Fig. 2). The anode and cathode, both consisting of two platinum meshes of surface areas of 2.2 and 1 $cm^2$, respectively, were connected to a digital coulometer (Model 640, The Electrosynthesis Company, Inc, Amherst, NY, USA) to monitor the total electrical charge within the circuit during an 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. The G 750 potentiostat (Gamry Instrument, Warminster, PA, USA) equipped with a data acquisition system was used as the source of electrical current.

## Experimental Procedures

Pd-C powder catalyst suspended in an oil-formate solution under agitation was employed in the hydrogenation reaction. To initiate the reactions, 0.4 g of dodecyldimethylethyl ammonium bromide (EDDAB) (Xuanguang Co., Nanjin, China) as an emulsifier was added to the cathode chamber containing a mixture of 12.5 g refined and deodorized soybean oil (North Sea Oil and Grains Inc., Tianjin, China) and 58 g formate solution (Sigma Aldrich, St Louis, Mo, USA). Then 70 ml of 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 electric catalyst Pd-C at 5% (w/w) with a surface area of 900 $m^2/g$ (Dalian Toyounger Chemical Inc., Dalian, China) into the cathode chamber. A typical electrochemical oil hydrogenation process was performed when the electrical current (constant potential or constant current condition) was applied. The ranges of pH and formate concentrations tested were pH 2–10 and 0.4–2.4 M, respectively. Unless otherwise mentioned, 0.3 g Pd per 100 g oil was employed.

Upon completion of the reaction, the oil–water mixture (2.5 ml) was collected in a separatory funnel. Hexane (10 ml) and a saturated NaCl (ca. 5 ml) solution were added to the mixture, adequately vortexed and centrifuged (1,000×*g*) for 5 min. The supernatant containing the mixture of hexane and oil was pipetted, placed in 25 ml test tubes, oil was collected and vacuum-evaporated to remove hexane. Nearly 100% of the initial oil content was recovered by using this extraction procedure.

## Determination of Fatty Acids Composition

Methyl esters were prepared according to the official method AOCS Ce 2–66 [17] for determination of total *trans* fatty acids content and composition of fatty acids. The composition of the fatty acids was analyzed on a 6890N Network GC System gas chromatograph (Agilent Technologies, Palo Alto, Calif, USA) equipped with a flame ionization detector and a cold on-column injector. A capillary column HP-88 (100 m × 0.25 mm i.d.) coated with cyanopropyl-polysiloxane (film thickness of 0.2 μm) (PN112–88A7, Agilent Technologies) was used. Hydrogen (purity > 99.9997%) was used as the carrier gas and was maintained at a constant flow rate (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 employed as an internal standard to ensure a correct calculation of the fatty acid methyl esters in the samples. The injection volume of each sample was 1 μl. Analyses were conducted in duplicate and the sample means were reported. Twenty individual fatty acid methyl esters (FAMEs) 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 employed (Sigma Aldrich). The results were expressed in g per 100 g total fatty acid.

The total *trans* fatty acids content of foods were determined using Fourier transform infrared (FTIR) spectroscopy (AOCS Cd 14-95). A Nicolet Avatar 370 Infrared Spectrometer (Nicolet Instrument Corp., Madison, Wis, USA) was used. FTIR spectra between 900 and 1,050 $cm^{-1}$ were captured and the peak area under 966 $cm^{-1}$ was used for quantification of TFAs. A standard curve was established by using methyl elaidate ($C_{18:1}$ t-9) standards (Sigma Aldrich). All samples were thermostated 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 for iodine value (IV) and acid value (AV) according to official AOCS methods Cd 1c-85 and 5a-40, respectively. The hydrogenation selectivity of linolenic acid (SLn) and linoleic acid (SLo) were computed from the rate constants for the sequential hydrogenation of triene and diene fatty acids (reaction 1), as determined from the initial and final fatty acid profiles of soybean oil samples and from first-order rate expression for fatty acid hydrogenation [18]:

$$\text{trienes} \xrightarrow{K1} \text{dienes} \xrightarrow{K2} \text{monoenes} \xrightarrow{K3} \text{saturated} \qquad (1)$$

$$\mathrm{SLn} = {}^{K1}\!/_{K2} \qquad (2)$$

$$\mathrm{SLo} = {}^{K2}\!/_{K3} \qquad (3)$$

in which $K1$, $K2$, $K3$ are reaction rate constants in the process. The specific *trans* isomerization index (SII), which

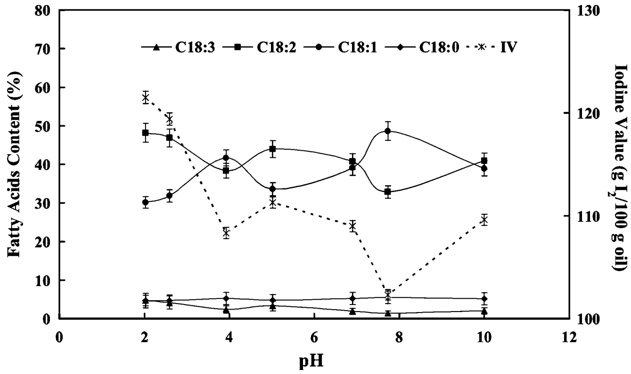

**Fig. 3** Effect of electrolyte pH on hydrogenated soybean oil (0.4 M formate, 0.3 g Pd/100 g oil, 0.02 g EDDAB/g oil, current density 10 mA/cm$^2$, 60 °C, 6 h, and 650 rpm)

is defined as the percentage increase in TFA content per unit change in the oil's IV, was also investigated [18].

$$\text{SII} = \%\ \text{increase in trans isomers/change in oil IV} \quad (4)$$

In addition, the current efficiency (CE) for oil hydrogenation was determined from the change in total moles of double bonds in the oil/fatty acid reactant and the total charge passed in the electrolysis [13].

$$\text{CE}\ (\%) = 100\big(\text{change moles of double bonds} \times 2\ \text{equiv per mole}\big) \times {}^{F}\!/_{Q} \quad (5)$$

where $F$ is Faraday's constant, $Q$ is the total charge passed in an experiment, which is the electric current integrated over time.

## Statistical Analysis

The processing parameters involved in the hydrogenation process were evaluated based on three replicates and the sample means were reported. All analytical measurements were conducted in triplicate unless otherwise stated. Data were analyzed using SPSS (SPSS for Windows, Version Rel. 10.0.5, 1999, SPSS Inc., 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. Significances from post hoc analysis are reported ($P < 0.05$).

# Results and Discussion

## Effects of pH

The pH of the electrolyte formate solution was found to significantly affect the extent of hydrogenation and the fatty acid profile (Fig. 3). The concentration profile of individual fatty acids was found to vary as the pH changed from 2 to 10, whereas the IV values gradually decreased as pH increased, with two abrupt dips at pH 4.0 and 7.6, resulting in a peak on the IV curve at pH 5.0. It is intriguing to note that the IV peak at pH 5.0 corresponded to the lowest content of *trans* isomers and SII at the same pH (Table 1). Moreover, the reduced linolenic acid selectivity (SLn) and increased linoleic acid selectivity (SLo) were also observed at pH 4.0 and 7.6, indicating that the hydrogenation rate of diene was promoted. The acid value (AV) of the product was found to reach below 1.0 mg KOH/g when the pH of the electrolyte was kept between 5.0 and 7.6. Contrarily, a higher AV of hydrogenated oil was observed at pH < 5.0 or >7.6. Such pH dependency as well as the peaks and valleys of the degree of hydrogenation could possibly be attributed to two different reaction mechanisms within the range of pH investigated.

**Table 1** Effect of electrolyte pH on *trans* fatty acids content (TFAs), specific isomerization index (SII), hydrogenation selectivity of SLn and SLo, and free fatty acid value (AV)

| pH | TFAs[a] (% fat, w/w) | SII | SLn | SLo | AV (mg KOH/g oil) |
|---|---|---|---|---|---|
| 2.0 | 19.6d ± 0.1 | 2.04d ± 0.12 | 2.55a ± 0.07 | 3.81a ± 0.18 | 2.43d ± 0.09 |
| 2.5 | 27.1e ± 0.3 | 2.33d ± 0.25 | 2.61a ± 0.15 | 4.41b ± 0.18 | 1.91c ± 0.02 |
| 4.0 | 29.7f ± 0.1 | 1.29c ± 0.08 | 2.47a ± 0.18 | 8.66d ± 0.07 | 1.05b ± 0.11 |
| 5.0 | 6.5a ± 0.2 | 0.38a ± 0.07 | 3.12b ± 0.06 | 3.89a ± 0.05 | 0.70a ± 0.07 |
| 7.0 | 15.4b ± 0.1 | 0.67ab ± 0.04 | 3.39b ± 0.10 | 5.22c ± 0.31 | 0.79a ± 0.10 |
| 7.6 | 32.8g ± 0.4 | 1.12c ± 0.12 | 2.60a ± 0.11 | 19.82e ± 0.14 | 0.83ab ± 0.13 |
| 10.0 | 16.7c ± 0.1 | 0.75b ± 0.06 | 3.30b ± 0.02 | 5.48c ± 0.02 | 1.08b ± 0.10 |

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

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

*SII* % increase in *trans* isomers/change in oil iodine value (IV)

*SLn* is linolenate selectivity

*SLo* is linoleate selectivity

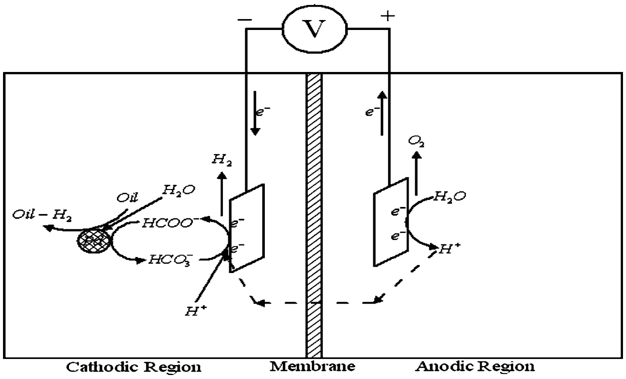

**Fig. 4** Principle of the diaphragm hydrogenation with formate

Inside the electrochemical reactor where reduction and oxidation reactions occur at the cathode and anode, respectively, the electrons move from the anode to the cathode via the circuit and the protons migrate through the Nafion 117 cation membrane to the cathode under the applied current (Fig. 4). In the present study, $H_2O$ is electrochemically oxidized to electrons and protons at the anode area as shown in reaction (6):

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{6}$$

Meanwhile, in the cathode chamber, the sequential chemical reactions between the formate ions and unsaturated fatty acids of oil in the presence of Pd as a hydrogenation catalyst occur (as shown in reactions 7, 8), and the overall oil hydrogenation reaction could be summarized (reaction 9) [11]:

$$HCOO^- + H_2O + Pd \rightarrow H\,Pd\,H + HCO_3^- \tag{7}$$

$$H\,Pd\,H + Oil \rightarrow Oil\,H_2 + Pd \tag{8}$$

$$HCOO^- + H_2O + Oil \xrightarrow{Pd} Oil\,H_2 + HCO_3^- \tag{9}$$

The product bicarbonate ions of reaction (9) can then be reduced electrochemically to formate ions at low pH on the surface of cathode, which regenerates the formate ions (reaction 10) [14]:

$$HCO_3^- + 2H^+ + 2e^- \rightarrow HCOO^- + H_2O \tag{10}$$

However, the unwanted side reactions of releasing hydrogen (reaction 11) and carbon dioxide (reaction 12) will be enhanced at lower pH, which could limit the transport of bicarbonate ions to the electrode and impede the regeneration of formate ions at the cathode:

$$2H^+ + 2e^- \rightarrow H_2 \tag{11}$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O \tag{12}$$

When the reagents—oil, mediator solution, and catalyst—gather at the same location at the same time, the electrochemical hydrogenation reaction starts. Therefore, the hydrogenation process in question can be separated into two stages based on the changes of IV (Fig. 3). The first being the low pH stage (pH 2–5) where formate ion regeneration controls the extent of hydrogenation. As the pH increases to 5–10 (the high pH stage), the hydrogenation process is influenced primarily by the formate ion stability.

Experimentally, the rate of regeneration of formate ions was found to be the most at pH 4.0, as evidenced by the low IV (Fig. 3) that represents a high degree of hydrogenation. This result corresponded well with those reported in the literature [14]. On the other hand, the relatively low value of SLn (2.47) indicates that a high concentration of hydrogen donors was present on the surface of catalyst during the reaction [18], whereas the high value of SLo (8.66) signifies the accelerated hydrogenation rate of $C_{18:2}$ at pH 4.0, as indicated by Eq. (3). However, under fairly acidic conditions ($pH < 4.0$), not only was hydrogen gas found to evolve at the cathode and consequently limited the mass transport, but the formation of $CO_2$ was expected to be enhanced in a more acidic solution ($pH < 3.5$) according to reaction (12). Furthermore, besides the formations of $H_2$ and $CO_2$, more formic acid and bicarbonate acid will be present in the acidic electrolyte due to the following chemical equilibriums (reactions 13, 14), where the regeneration of formate ions is further inhibited due to the reduction in the number of formate ions in hydrogenation.

$$HCOO^- + H^+ \leftrightarrow HCOOH \tag{13}$$

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \tag{14}$$

As the pH increased above 4.0, since fewer protons are produced to maintain the regeneration of formate ions, it could be postulated that the extent of hydrogenation was solely dependent on the stability of the formate ions.

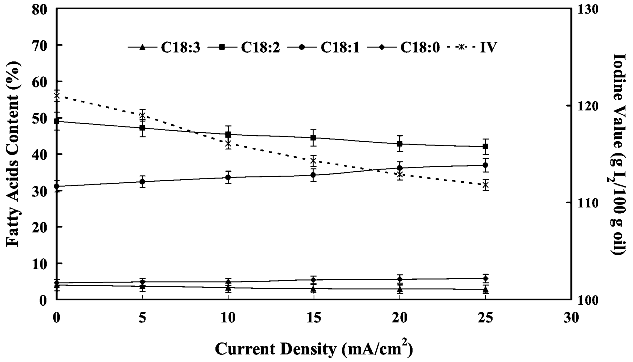

**Fig. 5** Effect of current density on hydrogenated soybean oil (0.4 M formate, 0.3 g Pd/100 g oil, 0.02 g EDDAB/g oil, pH 5.0, 60 °C, 6 h, and 650 rpm)

**Table 2** Effect of current density on *trans* fatty acids content (TFAs), specific isomerization index (SII), hydrogenation selectivity of SLn and SLo, and current efficiency (CE)

| Current density (mA/cm$^2$) | TFAs[a] (% fat, w/w) | SII | SLn | SLo | CE (%) |
|---|---|---|---|---|---|
| 0 | 7.2d ± 0.3 | 0.69b ± 0.09 | 3.69d ± 0.03 | 0.95a ± 0.04 | |
| 5 | 4.0a ± 0.2 | 0.34a ± 0.04 | 3.24c ± 0.04 | 6.33e ± 0.05 | 100 |
| 10 | 5.5b ± 0.4 | 0.38a ± 0.08 | 3.13c ± 0.02 | 3.89c ± 0.02 | 100 |
| 15 | 6.4c ± 0.2 | 0.39a ± 0.02 | 3.10c ± 0.11 | 3.27b ± 0.09 | 83 |
| 20 | 8.7e ± 0.1 | 0.44a ± 0.01 | 2.90b ± 0.05 | 4.26d ± 0.06 | 77 |
| 25 | 8.7e ± 0.1 | 0.41a ± 0.07 | 2.71a ± 0.03 | 4.42d ± 0.04 | 65 |

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, 6 h, and 650 rpm

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

*CE* (%) 100 (change moles of double bonds × 2 equiv per mole) × $F/Q$, $F$ is Faraday's constant, $Q$ is the total charge passed (integration of electric current over time) in an experiment

Sodium formate, a salt derived from a weak acid and a strong base that contains the most abundant free formate ions, is more stable in weak alkali electrolytes than in acidic, so are the bicarbonate ions [19]. This explains why the lowest IV and the largest extent of hydrogenation were reached at pH 7.6 (Fig. 3). Under stronger alkali electrolytes ($pH > 7.6$), the hydrogenation reaction was hindered as indicated by the increased IV (Fig. 3) due mainly to catalyst poisoning that could take place when fatty acids react with sodium hydroxide to form soap [20].

To date, there have been few studies in the literature concerning the effect of electrolyte pH associated with the free fatty acids present on electrochemical hydrogenation. With regard to the quality of hydrogenated oil, finished products with low AV are preferred [20], and the degree of oil hydrolysis would increase if excessive acids or bases were added in the reaction. Compared with other electrochemistry studies [14, 21], the present study employed formic acid in the reaction system at a level of 0.4 M, which was 25–43% less than those reported in the literature [14, 21]. The unique design integrating the PEM with the electrodes enabled the hydrogen proton donors to transfer protons through the PEM from anode to cathode to maintain the supply of protons, keeping the AV low in the products.

## Effects of Current Density

Since electrochemical hydrogenation could not be performed without a current, and a positive correlation between the total number of electrons and regeneration of formate ions has been identified [14]. The influence of current density on electrochemical hydrogenation of oil is critical in assessing the performance of the process. As the extent of hydrogenation was increased by increasing current density (Fig. 5), the IV decreased 16% when current density increased up to 25 mA/cm$^2$. Theoretically, the percentage of IV reduction (compared to zero current) is reflective of the percentage of formate ions regenerated. However, due to all the reactions going on, regeneration of formate at a current density of 25 mA/cm$^2$ could only reach less than the calculated value (16%).

Moreover, the lowest value of *trans* isomers and SII was found at a current density of 5 mA/cm$^2$ (Table 2), reducing the *trans* fatty acids and SII by 24 and 50%, respectively. The resulting 100% current efficiency at low current densities (5–10 mA/cm$^2$) suggests that further increase in current density above 10 mA/cm$^2$ did not contribute proportionally to the hydrogenation process, and was possibly involved in undesired side reactions [14, 15].

## Effects of Formate Ion Concentration

As seen in Fig. 6, increases in the concentration of formate ions in the reaction from 0.4 to 2.5 mol/L resulted in a rapid decline in the IV (ca. 31.6%). Whereas, almost complete hydrogenation of linolenate ($C_{18:3}$) was achieved

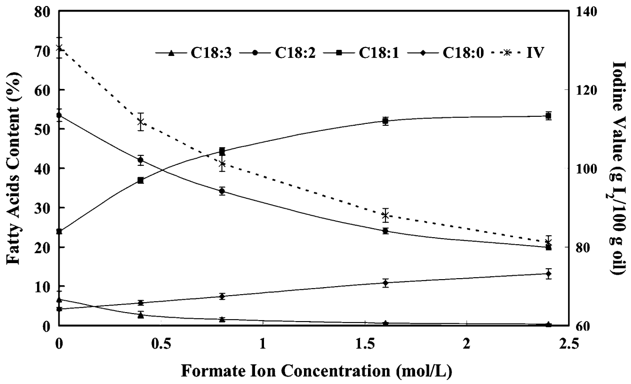

**Fig. 6** Effect of formate ion concentration on hydrogenated soybean oil (0.3 g Pd/100 g oil, 0.02 g EDDAB/g oil, pH 5.0, 60 °C, current density 25 mA/cm$^2$, 6 h, and 650 rpm)

**Table 3** Effect of formate ion concentration on *trans* fatty acids content (TFAs), specific isomerization index (SII), and hydrogenation selectivity of SLn and SLo

| Formate ion concentration (mol/L) | TFAs[a] (% fat, w/w) | SII | SLn | SLo | CE (%) |
|---|---|---|---|---|---|
| 0.4 | 7.7a ± 0.2 | 0.41 ± 0.04 | 2.71 ± 0.06 | 4.42a ± 0.02 | 65 |
| 0.8 | 11.4b ± 0.1 | 0.39 ± 0.03 | 2.61 ± 0.03 | 4.94b ± 0.04 | 78 |
| 1.6 | 14.9c ± 0.3 | 0.35 ± 0.07 | 2.53 ± 0.03 | 5.25c ± 0.01 | 87 |
| 2.4 | 16.5d ± 0.2 | 0.33 ± 0.04 | 2.51 ± 0.01 | 5.67d ± 0.02 | 93 |

Experimental conditions were 0.3 g Pd/100 g oil, 0.02 g EDDAB/g oil, pH 5.0, 60 °C, current density 25 mA/cm$^2$, 6 h, and 650 rpm

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

with a concomitant decrease in linoleate ($C_{18:2}$), accompanied by simultaneous increases in the stearate ($C_{18:0}$) and oleate ($C_{18:1}$) contents. The *trans* isomer content significantly increased from 7.7 to 16.5% and the specific *trans* isomerization index (SII) decreased from 0.41 to 0.33% (Table 3), whereas the reaction selectivity of SLn slightly decreased and SLo increased. These data indicated that the extent of hydrogenation was positively dependant on the concentration of formate ions, in agreement with the studies conducted on catalytic transfer hydrogenation of vegetable oils [22] and soybean lecithin [23].

In fact, the reaction was processed via competitive adsorption of water and formate ions on identical active sites on the catalyst surface [14]. Because of the sufficient water supplied in the reaction, elevated concentrations of sodium formate could be employed, allowing more hydrogen donors (the combination of formate and water) to be formed on the surface of the catalyst, which in turn resulted in the decreased *trans* isomer generating rate (SII) (Table 3). In addition, it could also be seen in Table 3 that the increase of formate ion concentration led to higher current efficiency, which could be attributed to more electrons absorption by the bicarbonate ion. However, it should be noted that the extent of hydrogenation would in fact decrease with excessive formate ions because the emulsion of oil and water could be destroyed by the salting-out effect [23]. Therefore, selection of the proper electrolyte is critical, since a strong electrolyte could change the emulsifying agent EDDAB and the interfacial area of oil–water, resulting in disruption of their surface ionization states.

## Effects of Temperature

Similar to other electrochemical reactions, temperature is the most crucial parameter in the attempt to produce hydrogenated oil with reduced *trans* fatty acids [14, 21]. Using the setup developed in the present study, no hydrogenation was found at temperatures lower than 45 °C, as indicated by the same fatty acid composition as that of the original oil (Fig. 7). As the processing temperature increased from 45 to 75 °C, the IV of the oil was found to decline sharply, resulting from increases in $C_{18:0}$ and $C_{18:1}$ contents while both $C_{18:2}$ and $C_{18:3}$ decreased. Evidenced by the increases of TFAs from 4.3% at 45 °C to 20.7% at 75 °C (Table 4), it is clear that the temperature under which the hydrogenation process took place was not only associated with the extent of the reaction but also significantly altered the composition of *trans*- and *cis*-fatty acids in the finished oil. According to the Arrhenius equation that denotes the relationship between temperature and corresponding rate constants, it is well recognized that high temperature enhances the reaction rate, and hence the production of TFAs were favored at a high operation temperature regardless of the method used for hydrogenation [18].

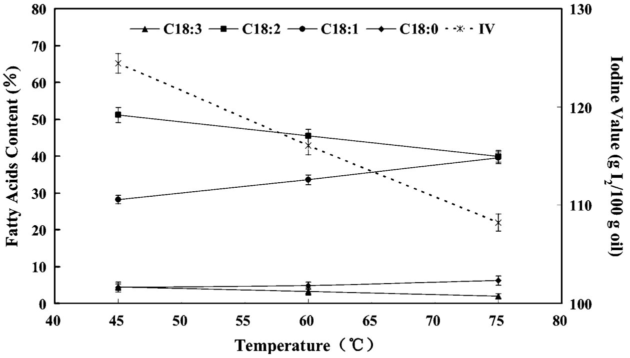

**Fig. 7** Effect of temperature on hydrogenated soybean oil (0.4 M formate, 0.3 g Pd/100 g oil, 0.02 g EDDAB/g oil, pH 5.0, current density 10 mA/cm$^2$, 6 h, and 650 rpm)

On the other hand, as seen in Table 4, the lowest SII value (0.38) was observed at 60 °C, whereas significant reductions in reaction selectivity SLn and SLo were found when the temperature was raised from 45 to 60 °C, suggesting that the highest hydrogenation rate occurred during the conversion of $C_{18:1}$ to $C_{18:0}$. These results were in agreement with the findings reported by An et al. [13], who suggested that the reaction rate of TFAs was significantly lower than that of the hydrogenation reaction at 60 °C. However, an additional increase in temperature up to 75 °C resulted in accelerated *trans* isomerization to a greater

**Table 4** Effect of temperature on *trans* fatty acids content (TFAs), specific isomerization index (SII), and hydrogenation selectivity of SLn and SLo

| Temperature (°C) | TFAs[a] (% fat, w/w) | SII | SLn | SLo |
|---|---|---|---|---|
| 45 | 4.3a ± 0.1 | 0.54a ± 0.06 | 4.46b ± 0.03 | 11.08c ± 0.08 |
| 60 | 6.5b ± 0.2 | 0.38a ± 0.09 | 3.12a ± 0.02 | 3.89a ± 0.09 |
| 75 | 20.7c ± 0.1 | 0.88b ± 0.10 | 3.11a ± 0.04 | 4.83b ± 0.05 |

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

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

extent than the oil hydrogenation, which led to a significant increase of SII. Therefore, to produce highly hydrogenated oil with low TFAs, the processes should be controlled at 60 °C. A similar observation was reported using a different reactor [21].

## Effect of Catalyst Loading

A Pd-C powder catalyst suspended in an oil-formate solution under agitation was employed in the hydrogenation reaction due primarily to its unique catalytic activity, namely the acclaimed ability to produce less geometrical and positional isomers at a rate 30–100 times greater than nickel and other commercially available hydrogenation catalysts [20]. As seen in Fig. 8, a 25% decrease in the IV was found when the catalyst loading was increased from 0.1 to 0.8% (Pd in oil, w/w). When Pd loading was less than 0.1% of oil, its catalytic effect was negligible. Such phenomena could be attributed to the existence of multiple controlling mechanisms in the reaction. It is postulated that, at low loadings (0–0.1%) of the catalyst, the small molecules (formate ions and water) occupied the surface of Pd-C, blocking triglycerides. Since the formate ions and water acted in bulk, the oil could not be easily dispersed in the aqueous solution. The absence of oil on the surface of the catalyst prevented the hydrogenation reaction from occurring.

When the catalyst loading was at above 0.1% of oil, especially in the range of 0.1–0.2%, the oil could gradually be absorbed onto the surface of the catalyst, resulting in elevated levels of hydrogenation (Table 5). Furthermore, it was notable that the SII stayed relatively flat with further increase of catalyst loading above 0.2%, which suggests that additional active sites were made available by the catalyst and subsequently decreased the desorption rate of hydrogen atoms on the catalyst surface, and thus directly reduced the occurrence of *trans* isomers while the high hydrogenation rate was maintained. On the other hand, while the TFAs continued to increase with increasing catalyst loading, for the hydrogenation selectivity the value of SLn was found to decrease significantly with increasing catalyst loading, contrary to the increase in SLo, indicating that the reduction reaction from linoleate to oleate was further accelerated when more catalyst became available.

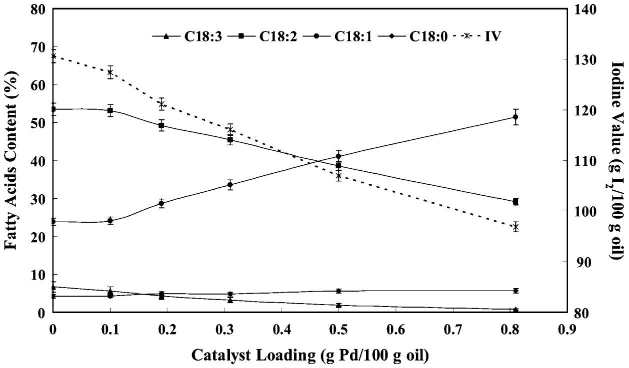

**Fig. 8** Effect of catalyst loading on hydrogenated soybean oil (0.4 M formate, 0.02 g EDDAB/g oil, pH 5.0, 60 °C, current density 10 mA/cm$^2$, 6 h, and 650 rpm)

## Effect of Agitation

The effect of agitation speed on the reaction process was investigated in terms of IV and the compositions of hydrogenation oil (Fig. 9). A slight decrease (ca. 5%) of IV from 130.04 to 123.42 g $I_2$ per 100 g oil was observed at an agitation speed of 450 rpm, and a total of approximately 25% reduction of IV was found when the agitation speed was increased up to 820 rpm. The degree of hydrogenation, as indicated by the increased stearic acid content, was improved with increasing agitation. From the composition standpoint, a rapid decrease in the specific *trans* isomerization index (SII) was found when agitation increased from 450 to 820 rpm (Table 6). An obvious decrease of hydrogenation selectivity (SLn and SLo) was observed when the agitation speed was increased, especially from 650 to 820 rpm, indicating that increase in agitation speed beyond 820 rpm might further reduce the hydrogenation selectivity. Therefore, additional investigations are needed to characterize hydrogenation under agitations higher than those investigated, since it is critical to control how the hydrogen atoms migrate under vigorous agitation.

**Table 5** Effect of catalyst loading on *trans* fatty acids content (TFAs), specific isomerization index (SII), and hydrogenation selectivity of 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, pH 5.0, 60 °C, current density 10 mA/cm$^2$, reaction time 6 h, and 650 rpm

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

## Quality of Soybean Oil Produced

Electrochemical hydrogenation using formate ions as the mediator in the diaphragm reactor was performed under controlled conditions. A significant reduction (32%) of the iodine value and an increase in TFAs were observed in the hydrogenated soybean oil (Table 7), which means a specific isomerization index SII of 0.17 was achieved. The processing temperature (60 °C) employed in the present study was much lower than the 220 °C used with the conventional nickel catalysts using standard pressurized gas hydrogenation conditions, although it required a longer processing time (6 h vs. 100 min) [25]. Most importantly, the hydrogenated soybean oil produced contained only 8.62% TFAs, significantly lower than that reported in the commercial hydrogenation process (>45%) [25].

Compared with other electrochemical hydrogenation studies, the setup employed in the present study improved hydrogenation due mainly to the highly active Pd catalyst; a significant reduction in the level of formate ions added (25–43% less) was found to be capable of reaching a similar SII value to those reported in the literature [14, 21]. A low acid value (AV, 0.7 mg KOH/g oil) of the hydrogenated oil was in line with the soybean oil quality requirements [24]. Therefore, the experimental setup reported in the present study using PEM as the diaphragm was capable of reducing the level of formic acid addition, which directly leads to a low AV of the hydrogenated oil.

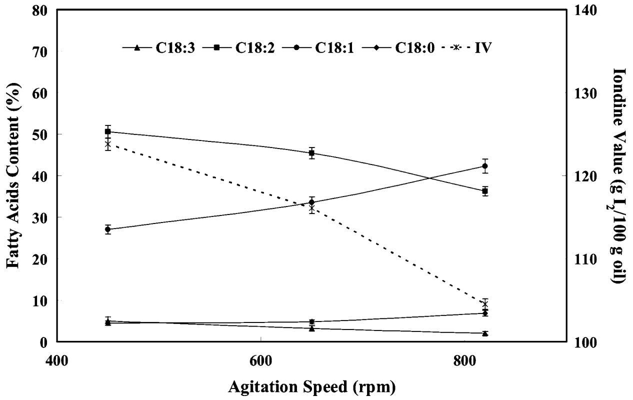

**Fig. 9** Effect of agitation speed on hydrogenated soybean oil (0.4 M formate, 0.3 g Pd/100 g oil, 0.02 g EDDAB/g oil, pH 5.0, 60 °C, current density 10 mA/cm$^2$, 6 h)

## Conclusion

Electrochemical hydrogenation in a diaphragm reactor using formate ions as the mediator and Pd-C as the catalyst was found to be adequate for producing hydrogenated soybean oil with a low AV under moderate processing temperature and atmospheric pressure. Various processing parameters, including current density, formate ion concentration, reaction temperature, catalyst loading, and speed of agitation, were found to influence the extent of hydrogenation. The hydrogenation process appeared to be controlled by two distinct mechanisms: (1) under low pH range (2.0–5.0) regeneration of formate ions was found to be crucial to the extent of hydrogenation and (2) as pH increased to 6.0–10.0, the hydrogenation process was dependent on the stability of the formate ions. A very low concentration (0.4 mol/L) of formate ions was therefore added to the reaction system since they could be continuously regenerated at the cathode. At the same time, the hydrogen proton donors were transferred through the proton exchange membrane from anode to cathode to maintain the supply of protons. Consequently, a high quality oil containing 8.62% TFAs with low AV (0.7 mg KOH/100 g oil) and IV (88.86 g I$_2$/100 g oil) was achieved.

**Table 6** Effect of agitation speed on (TFAs), specific isomerization index (SII), and hydrogenation selectivity of SLn and SLo

| Speed of agitation (rpm) | TFAs[a] (% fat, w/w) | SII | SLn | SLo |
|---|---|---|---|---|
| 450 | 4.1a ± 0.1 | 0.60c ± 0.06 | 3.34c ± 0.04 | 0.61c ± 0.03 |
| 650 | 5.5b ± 0.3 | 0.38b ± 0.07 | 3.12b ± 0.03 | 0.38b ± 0.01 |
| 820 | 6.3c ± 0.3 | 0.24a ± 0.02 | 2.45a ± 0.04 | 0.24a ± 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$^2$, 6 h

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

**Table 7** Fatty acid profile of soybean oil and the hydrogenated product

| Fatty acids | Soybean oil[a] | Hydrogenated soybean oil |
|---|---|---|
| $C_{16:0}$ (%)[b] | 10.87 ± 0.02 | 10.48 ± 0.01 |
| $C_{18:0}$ (%) | 4.35 ± 0.03 | 10.44 ± 0.02 |
| $C_{18:1}$ (%) | 20.68 ± 0.02 | 24.94 ± 0.03 |
| $C_{18:2}$ (%) | 54.15 ± 0.05 | 51.18 ± 0.04 |
| $C_{18:3}$ (%) | 7.39 ± 0.01 | 0.64 ± 0.02 |
| Trans isomers (%) | 1.00 ± 0.03 | 8.62 ± 0.12 |
| IV (g $I_2$/100 g oil) | 130.04 ± 0.35 | 88.86 ± 0.23 |
| AV (mg KOH/g oil) | 0.50 ± 0.001 | 0.70 ± 0.001 |

Hydrogenated product of soybean oil represented the electrochemical hydrogenation oil under the conditions of 14 ml soybean, 56 ml 0.4 mol/L formate ion solution, 0.8 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 820 rpm agitator speed

[a] Data were expressed as means ± SD ($n = 3$)

[b] Fatty acids content is expressed as g fatty acid per 100 g total oil

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