Electrochemical Hydrogenation of Canola Oil Using a Hydrogen Transfer Agent

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ABSTRACT: A novel low-temperature process for the electrochemical hydrogenation of canola oil is described. An emulsion of oil and water containing formic acid and a nickel hydrogenation catalyst, placed in the cathode compartment of an electrolysis cell and subjected to an electrical current, underwent hydrogenation at temperatures as low as 45°C. At these low temperatures of hydrogenation, the *trans* FA content of the hydrogenated canola oil was very low as compared with that of the edible oils hydrogenated by commercial processes using high temperature and high partial pressure of hydrogen gas. Because of its adverse health effects, a high *trans* FA content in edible oils is viewed as undesirable. In addition to the commercially available nickel supported on silica, amorphous nickel-phosphorus alloys supported on a variety of substrates were also used. Amorphous alloys are generally very corrosion resistant because of the absence of grain boundaries. A mechanism for hydrogenation using the hydrogen transfer agent of formic acid and its continuous regeneration at the cathode was evoked to explain the experimental data.

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KEY WORDS: Canola oil, cathode, electrochemical, hydrogenation, *trans* fatty acids.

Hydrogenation of edible oils in commercial gaseous processes involves elevated temperature (about 150–225°C) and high pressure (10–60 psig), which leads to excessive equipment costs and operational problems. High-temperature hydrogenation also favors the production of *trans* FA. Recent studies have implicated *trans* FA in increasing cholesterol levels in the blood and enhancing blood lipoprotein. There is also evidence that *trans* FA may be associated with the development and acceleration of coronary heart disease. The key to lowering the *trans* FA in edible oils is by accomplishing hydrogenation at low temperatures. The gaseous hydrogenation process is not effective at low temperatures. Electrochemical hydrogenation, on the other hand, can be carried out at these temperatures. Pintauro and coworkers (1–7) have shown that when an emulsion of soybean oil (or other edible oil) and water is placed in the cathode compartment of an electrolysis cell, the application of electrical current results in the formation of atomic hydrogen at 70°C. The atomic hydrogen formed is adsorbed onto a hydrogenation catalyst (Raney nickel) where it is then transferred to the oil, resulting in its reduction. The oil produced has a lower *trans* FA concentration than that obtained by gaseous hydrogenation processes, although the evolution of hydrogen gas by water electrolysis results in lower faradaic current efficiency. In other studies, Šmidovnik and colleagues (8,9) used sodium formate and other hydrogen donors to transfer hydrogen chemically to vegetable oils (soybean, corn, peanut, and olive) at temperatures as low as 50°C. In their approach, formate ion is converted to bicarbonate ion upon oxidation; thus, the reaction rate decreases with time, although large amounts of sodium formate (typically 15 g of oil in 40 mL of 6.5 M sodium formate) are used.

The present research involves the use of formic acid for the chemical hydrogenation of canola oil; however, the oxidized form of the formate ion (i.e., bicarbonate) is reduced electrochemically at the cathode to regenerate the formic acid. Because relatively little energy expenditure is needed for regeneration and because the rate of reduction of the bicarbonate ion is comparable to that of unsaturated FA *via* catalytic transfer hydrogenation, the amount of formic acid needed to hydrogenate vegetable oil chemically is very small.

Rapeseed is a source of edible oil in many parts of the world. In the 1980s, Canadian plant breeders developed a new rapeseed cultivar that yields oil low in erucic acid (10), with the Canadian rapeseed industry named canola. The oil obtained from this variety of rapeseed has a lower content of sulfur than traditional rapeseed oil. Canola oil with sulfur increases the amount of catalyst required if the oil has not been properly degummed, refined, and bleached (11). Even these processes cannot completely remove the residual phosphorus, sulfur, and coloring pigments of the oil. The remaining sulfur increases catalyst and hydrogen usage and changes the product selectivity by forming nickel-sulfur compounds on the surface of the catalyst that will have different selectivities and activities from those of active nickel (12). The problem is more acute when hydrogenation is carried out at high temperatures; therefore, electrochemical hydrogenation of canola oil at low temperatures appears to be a reasonable approach.

EXPERIMENTAL PROCEDURES

Oil hydrogenation was carried out in a batch reactor as shown in Figure 1. A 150-mL reactor with a height/diameter ratio of 2.95 was used. The anode chamber (counter electrode) occupied 8 mL of anolyte and was separated from the cathode chamber (working electrode) by a fine glass frit that prevented any oil from entering the anode chamber. Resistance to the dif-

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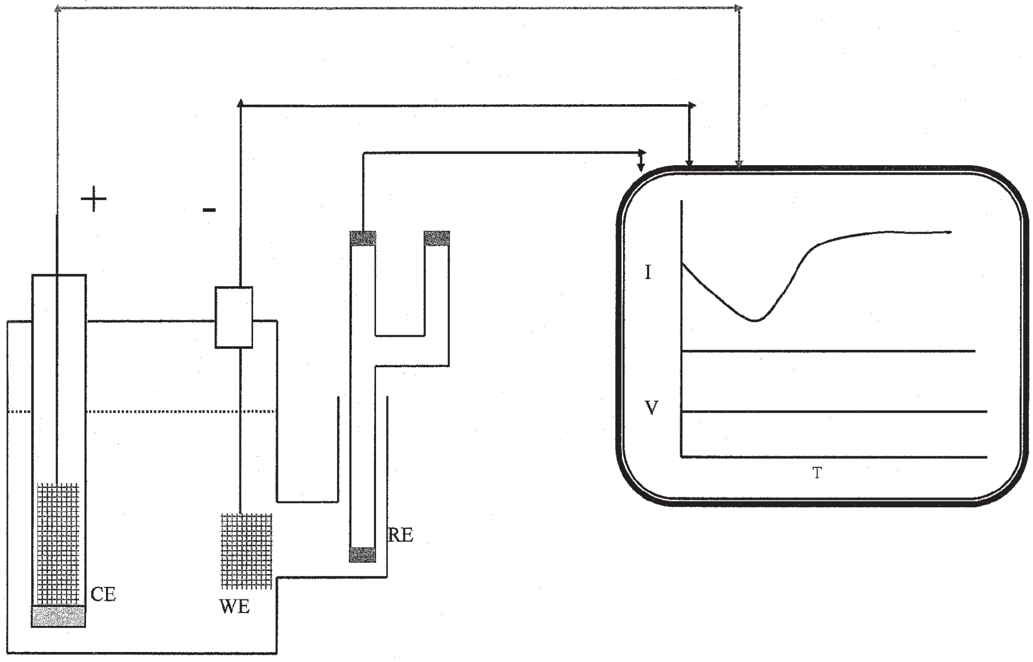


FIG. 1. Experimental setup. WE, working electrode; CE, counter electrode; RE, reference electrode.

fusion of ions across the membrane was negligible. Both the anode and cathode consisted of platinum mesh with surface areas of 2.25 and 1 cm^2, respectively. A magnetic stirrer provided agitation to disperse the oil in the electrolyte solution.

In a typical experiment, a predetermined amount of hydrogen transfer agent (i.e., electrocatalyst) was added to a mixture of oil and water. This was followed by the addition of the emulsifier, didodecyl diethyl ammonium bromide (DDAB). The oil/water/DDAB ratio was maintained at 0.23:0.77:0.0017 (by wt). The mixture was then stirred (with a magnetic stirrer) and heated to the specified temperature (45°C) in a water bath. The hydrogenation catalyst was then added. Preliminary experiments were conducted to identify the stirring rate that achieved maximal reduction of FA double bonds (under otherwise identical experimental conditions). Similar experiments were also conducted to determine the emulsifier concentration. A 750 potentiostat/galvanostat (Gamry Instruments) was used. Experiments were conducted for 12 h at constant electrode potential. At the conclusion of the experiment, the three-phase mixture was filtered through filter paper of pore size 2.5 µm to remove most of the aqueous phase as the filtrate. The oil-catalyst mixture was then collected and washed with *n*-heptane. The heptane layer was then centrifuged at 14.5 × *g* in a Marathon 8K Centrifuge (Fisher Scientific) for 30 min to separate the catalyst and any remaining water from the oil solution dissolved in *n*-heptane. After evaporation of the *n*-heptane, the oil sample was analyzed for composition. The use of this extraction procedure resulted in nearly 100% recovery of the initial oil.

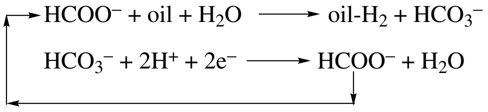
Materials. The unhydrogenated canola oil was obtained from Archer Daniels Midland Co. (Decatur, IL). The FA profile of the oil was as follows: 16:0, 7.21%; 18:0, 2.42%; 18:1, 52.36%; 18:2, 26.15%; 18:3, 11.15%; iodine value, 122.97; and *trans* FA, 0.98%. DDAB was obtained from Fluka (St. Louis, MO), and sodium formate (99.8%) and formic acids (97%) were obtained from Alfa Essar (Ward Hill, MA). Both sodium formate and formic acid are approved food-grade materials that have been used in past research to hydrogenate edible oils (8,9). Formic acid is used as a preservative and flavor adjunct (13). Formate is an intermediate in normal metabolism, and past studies have shown no cumulative toxic effects from its use. In addition, the U.S. Food and Drug Administration also has also approved the use of long-chain alkyl ammonium bromides, such as DDAB, for food applications, and other researchers (14) have used the compound in pharmaceutical applications (e.g., delivery of nucleic acids). Both the nickel catalyst (Degussa Corp., Calvert City, KY) and nickel-phosphorus (Ni-P) catalysts prepared in the laboratory were used for the hydrogenation of canola oil.

Preparation of Ni-P on supports. The supports were pretreated with 10 mM of tin chloride for 24 h. This was followed by another pretreatment in 10 mM of palladium chloride for 24 h. The treated particles were then immersed in a solution of 40 g/L of nickel chloride, 40 g/L of nickel sulfate, and 15 g/L of sodium hypophosphite. The temperature of the bath was raised to 65°C and 8 g/L of glycine was added. A spontaneous reaction occurred, resulting in deposition of nickel on the surface of the particles. The amorphous powder deposited on the glass was collected. This procedure resulted in a particle-size distribution in the range of 2.1–9.4 µm for the Ni-P amorphous powder [adapted from Mallory and Hajdu (15)]).

Determination of composition. Methyl esters of the initial oil sample and the hydrogenated product were prepared according to AOCS method Ce 2-66 (16). The esters were analyzed by GC in accordance with AOCS method Ce 1-62 (16). The iodine value was obtained both from the GC composition using AOCS method Cd 1c-85 (16) and by the use of an attenuated total reflectance (ATR)-FTIR spectrometer (17) supplied by Nicolet Analytical Instruments Inc. The total *trans* isomer content of the samples was determined by ATR-FTIR using AOCS method Cd 14d-96 (16). The nickel content in the oil was found by atomic absorption (AA) using a VGP 210 AA spectrophotometer (Buck Scientific) based on the method recommended by AOCS Ca 15-75 (16). The FFA content was determined by ATR-FTIR (18). The composition of Ni-P was obtained by dissolving the catalyst in strong acid. The solution was then tested for nickel using the Buck Scientific AA spectrophotometer. The wavelength used was 232 nm. The specific surface areas for the various catalysts were determined using the Nova analysis package developed by Quantachrome Instruments (Boynton Beach, FL). This instrument uses the Brunauer–Emmet–Teller method.

RESULTS AND DISCUSSION

We hypothesized that the reduction of double bonds occurred *via* a chemical reaction between the formate ion and oil at the surface of the hydrogenation catalyst used in this study. The oxidized form of the formate ion (i.e., bicarbonate ion) was then reduced electrochemically at the cathode, resulting in regeneration of the formate ion (Scheme 1).



SCHEME 1

The corresponding anodic reaction was assumed to be oxygen evolution from water under acidic conditions:

$$H_2O \longrightarrow 0.5\ O_2 + 2H^+ + 2e^- \qquad [1]$$

In addition, the reaction shown in Scheme 1 shifts to the right at low pH; hence, the rate of regeneration of formate ion is accelerated. Another cathodic reaction is the proton reduction resulting in hydrogen evolution *via* the following reaction:

$$2H^+ + 2e^- \longrightarrow H_2 \qquad [2]$$

In an experiment conducted with 0.5 M formic acid, emulsifier, and oil (with no applied potential) for 12 h, the iodine value of the oil was 120, as opposed to 100 obtained for an experiment conducted under identical conditions except that an electrode potential of –0.5 V vs. saturated calomel electrode (SCE) was impressed. This indicated that although hydrogenation occurred mainly *via* the chemical route, the amount of formic acid present was not sufficient to result in appreciable hydrogenation of the canola oil. Continuous electrochemical regeneration of the formic acid was needed to achieve the desired reduction in iodine value.

Preliminary experiments were conducted to determine the effect of process parameters such as pH and stirring rate. Because of the low pH (3.8) of the oil/formate/formic acid reaction mixture, TG hydrolysis was expected. The FFA content of the unreacted oil, as determined using ATR-FTIR spectroscopy (18), was 0.8%. The oil/water/formic acid emulsion was stirred in the reactor for 12 h under open-circuit conditions. The FFA content of the oil was 1.1 and 2.4% for experiments conducted at an emulsion pH of 3.8 and 1.5, respectively.

In another set of experiments, the influence of the stirring speed of the magnetic stirrer on the extent of oil hydrogenation was studied. In the absence of stirring, no reaction was observed. An increase in the stirring speed led to a corresponding increase in the reaction rate as measured by the iodine value (a measure of the extent of hydrogenation). The stirring speed used here is the one that corresponds to the maximum decrease in iodine value.

The influence of the reuse of electrolyte on hydrogenation was studied previously (19). Electrolysis of the oil–water emulsion in the presence of a Ni catalyst was carried out for 12 h. At the end of the experiment, the oil was separated from the emulsion and its FA profile was determined. The electrolyte was recovered and reused to hydrogenate a fresh batch of oil. This process was repeated twice. The data showed that the FA profile of the hydrogenated oil in all the experiments remained essentially invariant. We concluded from this observation that no significant nickel deactivation took place and that nearly complete removal of the transfer agent (formate anion) and the emulsifier (DDAB) from the oil–water emulsion was achieved.

Nickel hydrogenation catalyst. The influence of adding formic acid as a hydrogen transfer agent (also called an electrocatalyst or mediator) is shown in Figure 2. The iodine value, a measure of the extent of unsaturation, decreased with formic acid concentration for all three (1, 2, and 3 g/L) loadings of the commercially available nickel catalyst used. It must be noted that the lower the iodine value, the greater the extent of hydrogenation. The iodine value of unhydrogenated canola oil was 123, and it decreased significantly with an increase in formic acid content. An iodine value as low as 98 was observed in one experiment. Although the *trans* FA content increased from about 1% for the unhydrogenated canola oil owing to the addition of formic acid, it did not increase significantly above 4% even when the iodine value decreased by 20%. The total charge passed ranged from 566, 781, and 983 coulombs, respectively, for formic acid concentrations of 0.5, 0.75, and 1.0 M at an applied electrode potential of –0.5 V vs. SCE. The faradaic current efficiency increased with increasing formic acid concentration when soybean oil was hydrogenated electrochemically (19) under similar conditions. The current efficiencies for formic acid regeneration were estimated to be greater than 95% in these experiments. Although no such data are available for canola oil, we have no

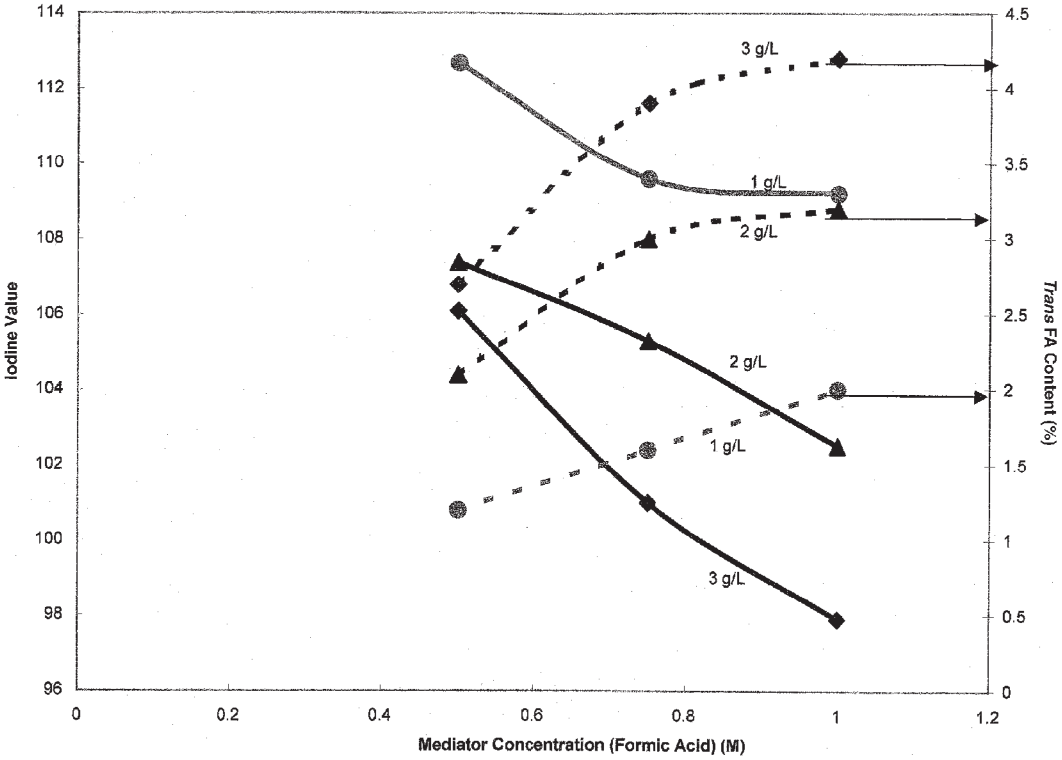


FIG. 2. Iodine value and *trans* FA content vs. hydrogen transfer agent for different catalyst loadings (g/L labels for the various plots refer to the catalyst loadings). Reaction conditions: –0.5 V vs. saturated calomel electrode (SCE), 45°C, 0.26 g didodecyl diethyl ammonium (DDAB), pH 3.8.

reason to believe that the current efficiency will not be similarly a function of formic acid concentration. For this set of experiments, the higher the nickel catalyst loading, the greater the extent of hydrogenation. The *trans* FA content increased with the extent of hydrogenation, a finding consistent with data on both gaseous and electrochemical hydrogenation of vegetable oils.

The influence of the nickel catalyst on the FA profile is shown in Figure 3. The data show that an increase in catalyst loading resulted in a decrease in linolenic and linoleic acid contents with a concomitant increase in oleic and stearic acid contents. The oleic acid content increased with catalyst loading, reached a maximum when 2 g/L of nickel catalyst was used, and then decreased with a further increase in catalyst loading. The data indicate that the hydrogenation reaction occurs primarily *via* a series pathway. Linolenic acid is hydrogenated to linoleic; linoleic acid to oleic; and oleic acid is converted to stearic. Thus, depending on the extent of hydrogenation, maximal concentrations of oleic and linoleic acids are to be expected at certain intermediate catalyst loadings. Experimental data bear out this hypothesis (Fig. 3). It is illustrative to compare the *trans* FA contents of the canola oil hydrogenated by electrochemical and gaseous hydrogenation processes (Ref. 20; Fig. 4). As expected, the data show that for both processes the *trans* FA content increased with a corresponding decrease in iodine value; nonetheless, the increase was rather steep for the gaseous hydrogenation process. On the other hand, for the electrochemical process described here, the *trans* FA content increased very slightly with the extent of hydrogenation. At the higher end of the extent of hydrogenation, the *trans* FA content of canola oil hydrogenated electrochemically was about one-eighth that obtained by the commercial gaseous hydrogenation process. Duplicates of selected experiments were performed. The average experimental errors were 2.3%, with values ranging from 2.1 to 4.0%. The oil–water emulsion used in this study had a low pH, which could have led to nickel dissolution. The presence of nickel in the aqueous phase was indeed observed (~1 ppm) at the end of experiments using AA spectroscopy. To effectively limit nickel dissolution, amorphous Ni-P alloys were deposited on various substrates, and subsequently their influence on the FA profiles of hydrogenated canola oil was studied as described below.

Ni-P alloy hydrogenation catalyst. Amorphous alloys are known to have excellent corrosion resistance. Corrosion generally occurs at grain boundaries; however, a lack of grain boundaries imparts enhanced corrosion resistance to amorphous alloys (21). Ni-P alloys were examined as hydrogenation catalysts in the experiments described below. Table 1 shows data on the phosphorus content in Ni-P electroless deposits and on a commercially available nickel hydrogenation catalyst on a silica support, along with their specific surface areas. The use of supports increases the effective surface area of the catalysts for the reaction and thus results in larger conversion values. Alumina and activated carbon have high surface areas and were thus chosen as supports for the new catalyst.

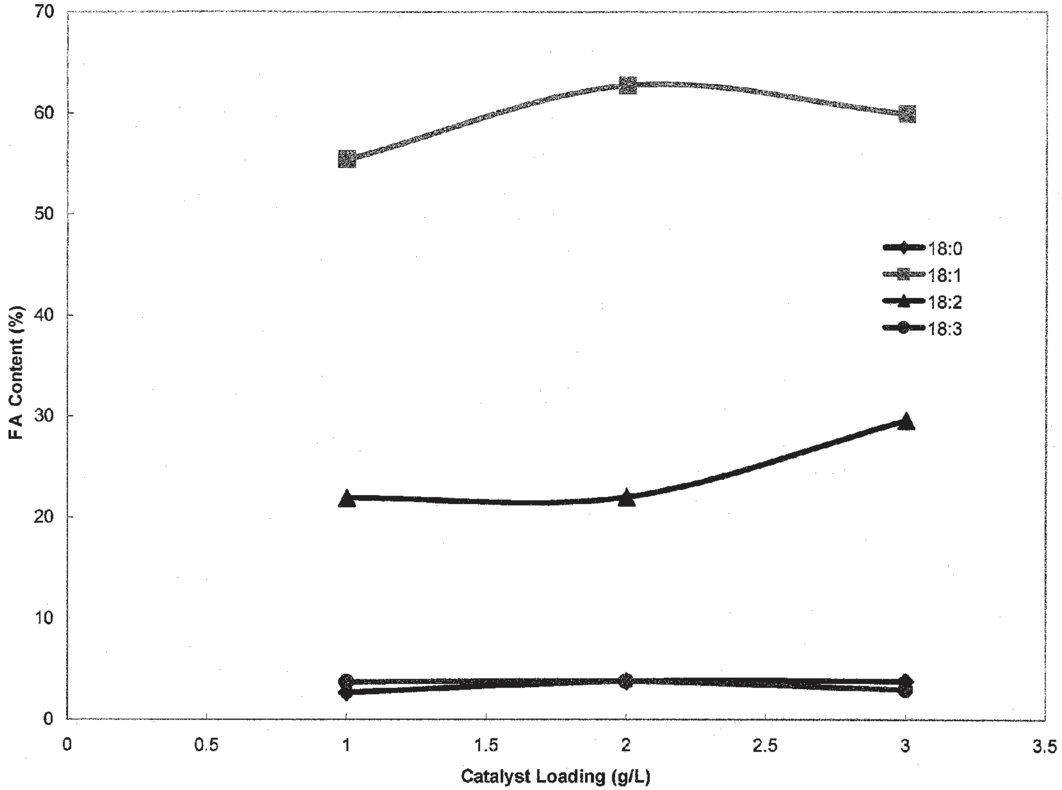


FIG. 3. FA profile vs. catalyst loading using 1 M hydrogen transfer agent (formic acid). Reaction conditions: –0.5 V vs. SCE, 45°C, 0.26 g DDAB, pH 3.8. See Figure 2 for abbreviations.

The data on hydrogenated canola oil are shown in Figure 5. The last column in each group contains the FA profile obtained by using the commercially available nickel catalyst (on a silica support). The data show that the extent of hydrogenation using amorphous alloys was comparable to that obtained using the commercial nickel catalyst. In addition, examination of the

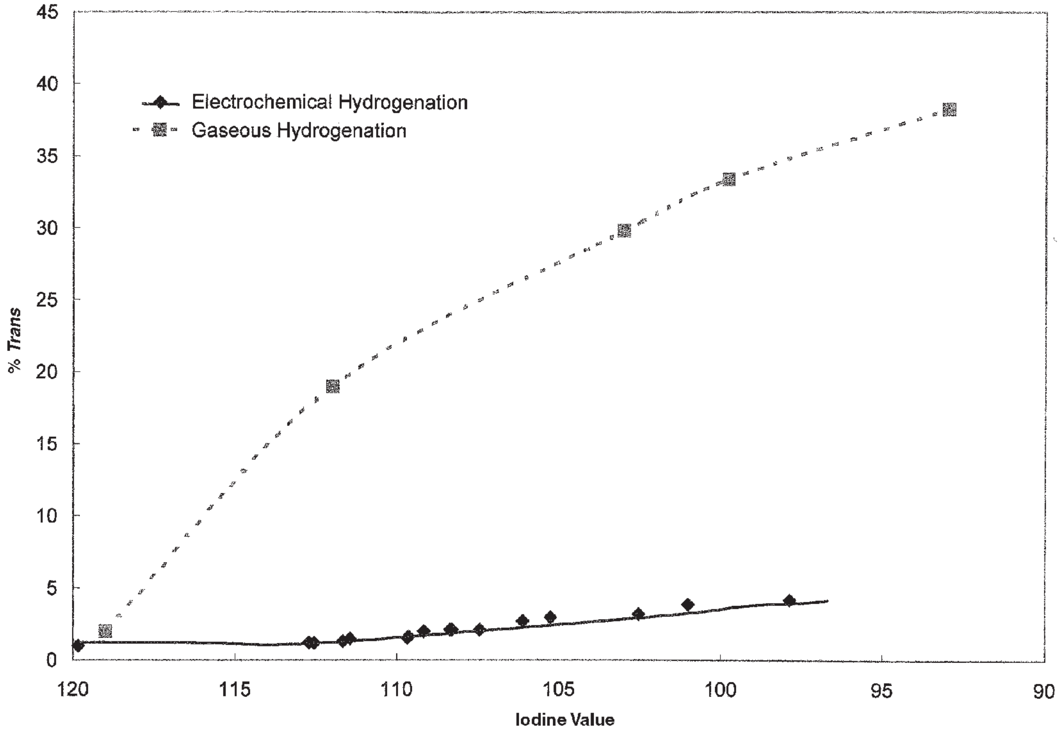


FIG. 4. *Trans* FA content (%) vs. iodine value. Data for gaseous hydrogenation from Köseoḡlu and Lusas (20).

TABLE 1
Characteristics of Laboratory-Prepared Ni-P Alloys and a Commercial Nickel Catalyst

Catalyst	P (% wt of Ni-P)	Ni (% wt overall)	Surface area (m^2/g)
Ni-P/carbon[a]	16.2	6.5	1071
Ni-P/alumina[a]	14.3	7.8	780
Ni-P powder[a]	53.6	46.4	29.4
Ni/silica[b]	0	7.1	770

[a] Prepared in the laboratory according to Mallory and Hajdu (15).
[b] Commercially available hydrogenation catalyst obtained from Degussa Corp. (Calvert City, KY).

surface area data provided in Table 1 indicates that the extent of hydrogenation, as evidenced by the iodine value, was directly proportional to the area of the catalyst used. As a result, the Ni-P powder (specific surface area of 29.4 m^2/g) showed a significantly lower extent of hydrogenation compared with the other catalysts (with specific surface areas greater than 770 m^2/g). The structure (or lack of it) of the catalyst did appear to have some influence on the selectivity of the individual FA hydrogenated. For example, the use of amorphous alloys, with the exception of the Ni-P powder, resulted in hydrogenated oil that had a significantly lower (up to 30%) *trans* FA content than that obtained using the commercially available crystalline nickel catalyst supported on silica. Of all the catalysts used in this study, Ni-P on a carbon support resulted in the highest oleic FA content and the lowest *trans* FA content. Less than 0.1 ppm Ni was observed in the used electrolyte for experiments carried out with the Ni-P catalysts supported on carbon and alumina, as opposed to 1 ppm Ni content noted for the experiments that involved the commercially available catalyst.

Mechanism of hydrogenation. There are two separate ways to hydrogenate canola oil by electrochemical methods. In the method described by Pintauro and coworkers (1,2), water electrolysis results in production of protons at the cathode. The protons are subsequently reduced to hydrogen gas. However, hydrogen is also adsorbed onto the hydrogenation catalyst surface (i.e., nickel), where it reduces the FA present in the vegetable oils. The dominant mechanism of hydrogenation in the present investigation involves the use of formic acid to transfer hydrogen to the canola oil (Scheme 1). Research (8) has shown that the formate ion can be used for hydrogenation of vegetable oils under the temperature conditions used in this study. One of the products of chemical reaction between the formate ion and vegetable oil in the presence of water is the bicarbonate anion. Previous work (22) has shown that under the application of mild cathodic potentials, formic acid is regenerated from the bicarbonate anion (Scheme 1). Thus, the concentration of formic acid in this study should remain fairly close to its concentration at the start of the experiment because formic acid is continuously regenerated at the cathode. In this study, compared with the one reported earlier (8), very small (up to 13 times lower) quantities of formate ion were used and a comparable extent of hydrogenation was obtained at lower temperatures. The molar ratio of formate ion to that of the double bonds used in this investigation was approximately equal to one.

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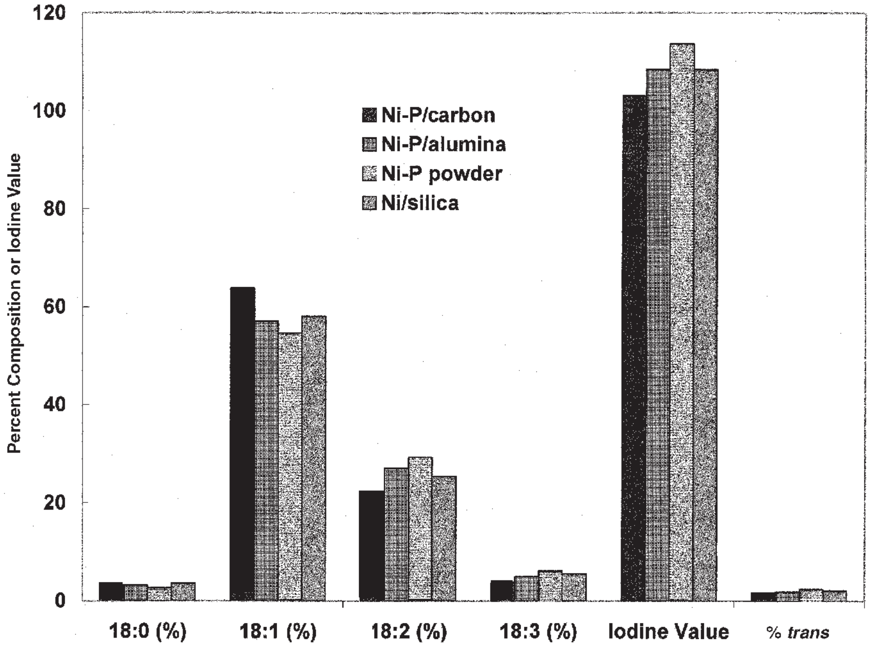

FIG. 5. FA distribution of hydrogenated canola oil using various nickel catalysts (–0.5 V vs. SCE, 45°C, 0.26 g DDAB, pH 3.8, 0.5 M formic acid, 1 g/L catalyst loading). See Figure 2 for abbreviations.

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