J Amer Oil Chem Soc (2007) 84:497–501
DOI 10.1007/s11746-007-1063-3

ORIGINAL PAPER

Low-*trans* Shortening and Spread Fats Produced by Electrochemical Hydrogenation

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Received: 3 July 2006 / Revised: 9 March 2007 / Accepted: 19 March 2007 / Published online: 24 April 2007

Abstract Partially hydrogenated soybean oils (90–110 IV) were prepared by electrochemical hydrogenation at a palladium/cobalt or palladium/iron cathode, moderate temperature (70–90 °C) and atmospheric pressure. The *trans* fatty acid (TFA) contents of 90–110 IV products ranged from 6.4 to13.8% and the amounts of stearic acid ranged from 8.8 to 15.4% (the higher stearic acid contents indicated that some reaction selectivity had been lost). The solid fat values and melting point data indicated that electrochemical hydrogenation provides a route to low-*trans* spreads and baking shortenings. Shortenings produced by conventional hydrogenation contain 12–25% *trans* fatty acids and up to 37% saturates, whereas shortening fats produced electrochemically had reduced TFA and saturate content. Electrochemical hydrogenation is also a promising route to low-*trans* spread and liquid margarine oils. Compared to commercial margarine/spread oils containing 8–12% TFA, the use of electrochemical hydrogenation results in about 4% TFA.

Keywords Soybean oil · Electrochemical hydrogenation · *trans*Fat · Shortening fats · Labeling requirements

Introduction

By January 1, 2006, the *trans* fatty acids (TFA) content had to be listed on food packaging. TFA contents of less than 0.5 TFA/serving may be declared as zero [1–3]. In view of the labeling regulations, there is much interest in technologies to decrease the contents of *trans* and saturated fatty acids in food products. These technologies include chemical and enzymatic interesterification, fractionation, blending of tropical fats with liquid oils, and genetic modification and plant breeding. Hydrogenation, the traditional technology of choice in fat modification, has also received some attention, including the use of noble metal catalysts, binary gas mixtures, supercritical conditions, and pressure controlled hydrogenation for TFA reduction [4].

Although electrochemical hydrogenation has been studied in the laboratory [5–10], little information has been published on the functional and physical properties of oils produced by this technology. Electrochemical hydrogenating edible oils employs a proton-exchange membrane (PEM) reactor, similar to that used in H_2/O_2 fuel cells, with water or H_2 gas as the source of hydrogen [5–9]. The key component of the reactor is a membrane–electrode-assembly (MEA), composed of catalytic precious metal powders for the anode and cathode that are hot-pressed as thin (fixed-bed) films onto the opposing surfaces of a Nafion® cation-exchange membrane (Nafion is a registered trademark of E. I. Du Pont de Nemours and Co., Inc., Wilmington, DE,

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USA). During reactor operation at a constant applied current with an anode feed of H_2 gas, H_2 molecules are oxidized electrochemically to H^+ and electrons. The electrons flow through the external electrical circuit to the cathode, whereas the protons migrate through the Nafion membrane under the influence of the applied electric field. When the protons contact the cathode, they combine with electrons to form atomic and molecular H_2 reduction products. Oil is circulated past the back-side of the cathode by means of a serpentine flow channel and the double bonds in unsaturated triglycerides react with the electro-generated hydrogen species. A schematic diagram of an MEA and the electrode reactions during electrochemical oil hydrogenation is shown in Fig. 1. Since the formation of atomic H and H_2 on the cathode catalyst is controlled by the applied current, the reaction can be carried out at a moderate temperature (i.e., 70–90 °C) and atmospheric pressure. Such low operating temperatures, in conjunction with the use of a precious metal cathode catalyst (e.g., Pt-black or Pd-black), results in partially hydrogenated oils with low amounts of *trans* fatty acids [6].

This paper describes the preparation of 90–110 IV soybean oils by using electrochemical hydrogenation and the evaluation of such oils as low-*trans* spreads and baking shortenings.

Experimental Procedures

Electrochemical Hydrogenation

Refined, bleached and deodorized soybean oil (132 IV) (C&T Refinery, Charlotte, NC, USA) was hydrogenated in the PEM reactor under constant current conditions (0.1 A/cm^2), atmospheric pressure, and either 70 or 90 °C temperature. MEAs with 25 cm^2 geometric electrode area were prepared using Pd-black powder as the cathode (at 2.0 mg/cm^2 loading) and Pt-black catalyst for the anode (0.5 mg/cm^2). These catalyst powders were mixed with a commercial solution of Nafion polymer and then coated on carbon cloth sheets (A-1 carbon cloth, 0.35-mm thickness, E-TEK, Inc., Somerset, NJ, USA). After thoroughly drying the electrodes, they were hot-pressed onto the opposing surfaces of a Nafion 117 cation-exchange membrane (approximately 175-μm dry thickness) with the catalyst layer directly contacting the membrane (Fig. 1). Previous studies have shown that the addition of Co or Fe to the Pd-black cathode improves hydrogenation selectivity [6, 8] and such bimetallic cathodes were employed in the present study. Co^{2+} or Fe^{2+} was loaded into the Nafion membrane by immersing the MEA in an aqueous solution of either 0.5 M $CoSO_4$ or 0.5 M $FeSO_4$ for 24 h. After thoroughly washing the MEA with water, sorbed cations (i.e., Co^{2+} or Fe^{2+} cations associated with the membrane's SO_3^- fixed charge sites) were then electroplated onto the Pd-black cathode of an MEA in the reactor before adding soybean oil reactant, as described elsewhere [6, 8]. In the present study, all bimetallic cathodes were composed of 1.0 mg/cm^2 of either Co or Fe deposited on 2.0 mg/cm^2 of Pd powder.

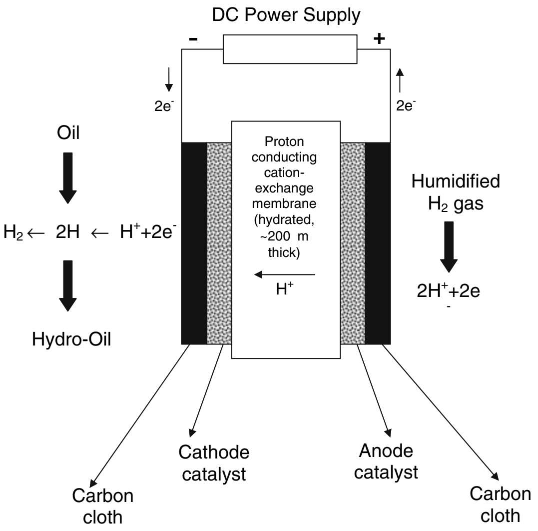

Fig. 1 Schematic diagram of the membrane–electrode-assembly and the relevant reactions in an electrochemical oil hydrogenation reactor

The PEM reactor was operated in batch recycle mode, where oil (~100 g) was continuously circulated through the reactor and into an external holding tank immersed in a constant temperature bath. The holding tank was continuously purged with N_2 gas to prevent oil oxidation. H_2 gas was bubbled through a water bottle, maintained at the reactor temperature, to achieve near 100% humidification prior to entering the reactor. Water vapor was used to hydrate the Nafion ion-exchange membrane, which can only conduct protons when fully sorbed with water. H_2 gas was purged after exiting the reactor. The oil flow rate was 140 ml/min and stainless-steel mesh turbulence promoters were inserted into the cathode feed channel to improve mass transfer of oil to/from the cathode [8]. The reactor temperature and H_2 flow rate/pressure were controlled by a fuel cell test station (Fuel Cell Technologies, Inc., Albuquerque, NM, USA). Periodically during hydrogenation, small oil samples were removed from the holding tank and the IV was estimated by determining refractive index. Hydrogenation was stopped when the oil IV reached a target value of 90, 100, or 110.

Chemical and Physical Analysis

Fatty acid compositions were determined by capillary gas–liquid chromatography. A Hewlett-Packard 5890 gas chromatograph (Wilmington, DE, USA) fitted with an

Table 1 Fatty acid compositions of electrochemically hydrogenated soybean oils (0.10 A/cm^2; 1.0 atm. H_2 pressure)

Cathode	Temperature (°C)	Fatty acid profile (%)				IV	Current efficiency (%)
		C18:0	C18:1	C18:2	C18:3		
Initial Oil		4.2	25.0	44.5	6.3	132	****
Pd–Co	70	14.4 13.7	42.5 44.4	29.0 28.7	2.1 1.5	92 92	71
Pd–Co	90	15.4	42.9	29.3	1.7	90	80
Pd–Fe	90	11.7	40.1	34.9	2.3	100	76

Table 2 Properties of electrochemically hydrogenated soybean oils

Catalyst	Temp (°C)	Iodine value	C18:1 *trans* (%)	Stearic acid (%)	NMR solids at temp (°C)					Dropping point (°C)
					10.0	21.1	26.7	33.3	40	
Pd–Co	90	90	12.6	15.4	24.7	17.3	16.8	13.9	9.4	47.5
Pd–Fe	90	90	13.6	15.2	25.4	17.5	16.4	13.4	8.9	47.3
Pd–Co	70	92	11.5	14.4	21.9	14.8	13.7	11.7	7.5	26.3
Pd–Co	90	100	10.0	13.3	18.7	13.1	12.4	10.6	7.5	49.5
Pd–Co	70	103	8.6	11.9	14.8	10.0	9.2	8.0	4.4	47.3
Pd–Fe	90	101	9.8	12.3	16.3	11.4	10.3	8.4	5.3	48.2
Pd–Fe	90	110	6.4	9.5	9.5	7.0	6.6	5.2	4.1	44.0
Pd–Co	90	110	6.5	10.3	11.5	8.4	7.5	6.3	4.1	45.8
Pd–Co	70	111	6.4	8.8	8.8	6.2	6.2	4.4	2.4	42.3

SP2330 column, 0.2-mm id, 0.2-μm film thickness (Supelco, Belafonte, PA, USA) was operated isothermally at 140 °C for 5 min, then temperature programmed to 230 °C at 20 °C/min. The detector temperature was 260 °C and the injector temperature was 250 °C.

Solid fat determinations were determined by pulsed NMR on a Bruker Minispec (Billerica, MA, USA) according to AOCS method Ce-1f-96 [10]. Mettler dropping points were determined according to the official AOCS method Cc-18-80 [10].

Results and Discussion

Representative examples of the fatty acid profiles for soybean oil partially hydrogenated in the electrochemical reactor are given in Table 1 for the Pd–Co cathode operating at 70 or 90 °C (IV 90) and for the Pd–Fe cathode at 90 °C (IV 100). In Table 1, current efficiency refers to the fraction of cathodically generated hydrogen that reacts with the oil. Current efficiencies <100% indicated that some electro-generated H_2 bubbled off the cathode as gas and was not available for hydrogenation. As can be seen, increasing the reaction temperature from 70 to 90 °C had little effect on the fatty acid profile of the IV 90 oil, but current efficiency increased from 71 to 80%. At constant current density (0.10 A/cm^2 in Table 1), the H_2 generation rate on the cathode was the same at both 70 and 90 °C, but the reaction rate was more rapid at the higher temperature. Thus, the concentration of unreacted H_2 on the Pd–Co cathode was lower at 90 °C than at 70 °C, which resulted in less H_2 formation and gas bubbling.

The reproducibility of the electrochemical hydrogenation process was illustrated by the fatty acid compositions of the two 92-IV oils for Pd–Co at 70 °C (Table 1). The 1–2% variation in the amounts of C18 fatty acids was typical. The fatty acid profile for 100-IV soybean oil that was hydrogenated at the Pd–Fe cathode was lower in C18:0 and C18:1 and higher in C18:2 and C18:3 contents than for 92-IV oils. The results for both the Pd–Fe and Pd–Co results show that: [1] the stearic and linolenic acid contents of electrochemically hydrogenated soybean oils were higher than those generated in a chemical catalytic reactor with a highly selective nickel catalyst; and [2] there was fast reaction of electrochemically generated H_2 and oil, even at the relatively moderate temperature of 70 °C, as indicated by the high hydrogenation current efficiencies (Table 1).

The properties of additional samples of electrochemically hydrogenated soybean oils are shown in Table 2. At iodine values ranging from 90–110, the *trans* fatty acids contents ranged from 6.4 to13.8%. Typically in heterogeneous hydrogenation with nickel catalysts (under selective

Table 3 Low-*trans* Spread Oils via Electrochemical Hydrogenation (111-IV soybean oil from Table 2)

Hydrogenation		Base (%)	Liquid oil (%)	Trans (%)	Solid fat at temp (°C)			Dropping point (°C)
Catalyst	Temp (°C)				10.0	21.1	33.3	
Pd–Co	70	70	30	4.2	6.0	4.3	3.1	37.4
Pd–Co	70	60	40	3.8	4.3	3.5	1.8	35.3

conditions), approximately 8–30% TFA were formed at 120 and 90 IV, respectively [11, 12]. Thus, about 57% reduction in TFA content was achieved with electrochemical hydrogenation. On the other hand, virtually no stearic acid was formed during selective hydrogenation, while electrochemical hydrogenation was accompanied by increased levels of stearic acid. After electrochemical hydrogenation, stearic acid increased from 4.4% in the unhydrogenated oil to 9–15%. The Pd/Co and Pd/Fe catalysts appeared to have similar properties with regard to *trans* and stearic acid formation.

The baking industry employs a number of shortening products, each of which is formulated to contain specified amounts of solid fat and melting points [13] (Fig. 2). Typical values for solid fat range 23–40% at 10 °C, 16–30% at 21.1 °C, 13–27% at 26.7 °C, 9–21% at 33.3 °C and 3–11% at 40 °C. Dropping points for baking shortenings range from 41 to 48 °C. TFA contents of commercial baking shortenings ranged from 12 to 25% and saturated acid levels are of the order of 27%. Thus, baking shortenings contain 39–52% of combined *trans* and saturated acids.

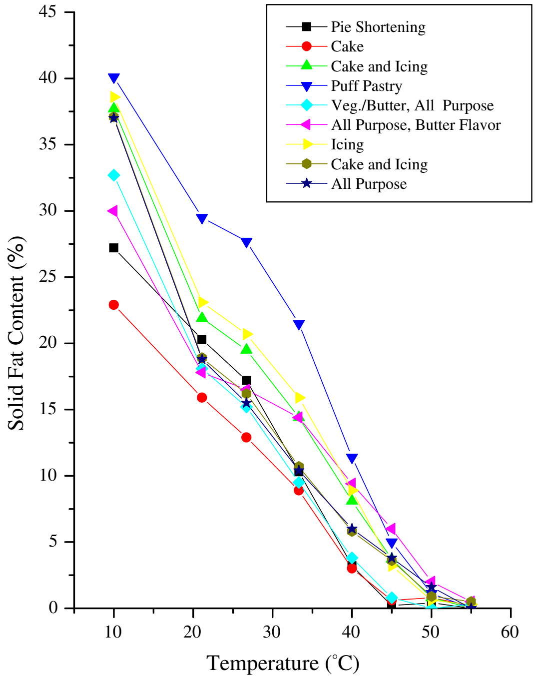

Fig. 2 Solid fat contents of commercial baking shortenings determined by pulsed NMR

The NMR solid profiles (Table 2) suggested that products prepared by electrochemical hydrogenation may serve as shortening fats. Another approach involves blending of the electrochemically hydrogenated oils with additional liquid oil and/or hardstocks. The dropping points (Table 2) closely matched those of commercial baking shortenings [13]. Electrochemically hydrogenated oils were evaluated as potential spread oils (Table 3). Compared to shortening fats having high, flat solid fat profiles, spread oils are formulated to have higher, sharp melting curves with melting points in the 32–33 °C range. Results shown in Table 3 indicated that low-*trans* spread oils containing about 4% TFA can be prepared by electrochemical hydrogenation. In addition, liquid margarines can be prepared with this technology. Typically, liquid margarine products have solid fat contents of 4–2 at 10 and 33.3 °C. Oils shown in Table 3 possess solid fat contents in this range [14].

Soybean oil has been electrochemically hydrogenated at moderate temperatures (70 and 90 °C) and atmospheric pressure at a Pd–Co or Pd–Fe cathode in a fuel-cell reactor. In this process, only oil and humidified hydrogen gas are fed to the reactor. Hydrogenated oil products in the range of 90–110 IV were characterized by having higher stearic acid content and lower amounts of *trans* fatty acids, compared to a traditional chemical catalytic scheme with nickel catalyst. The NMR solid fat profiles of product samples demonstrated that electrochemical hydrogenation offers a route to shortening fats, either directly as basestocks or as liquid oils that can be blended to produce the desired solid fat profiles. Additionally, the dropping points of the electrochemical hydrogenated oils closely match those of commercial baking shortenings. Low-*trans* spread oils containing about 4% total fatty acids can be prepared by electrochemical hydrogenation. Liquid margarines can be made using this technology with solid fat contents of 4–2 at 10 and 33.3 °C.

Acknowledgment This work was funded, in part, by the United Soybean Board. The authors thank Kevin Steidley (NCAUR) for experimental assistance.

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