JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 989–997

Electrocatalytic hydrogenation of soybean oil in a radial flow-through Raney nickel powder reactor

G. YUSEM, P. N. PINTAURO*, P.-C. CHENG, W. AN

Department of Chemical Engineering, Tulane University, New Orleans, Louisiana, 70118, USA

Received 25 September 1995; revised 23 December 1995

Soybean oil has been hydrogenated electrocatalytically on Raney nickel powder catalyst at atmospheric pressure and moderate temperatures in a novel undivided packed bed radial flow-through reactor. The reactor consisted of a single anode/cathode tubular element, where Raney nickel catalyst powder was contained in the annular space between two concentric porous ceramic tubes and the flow of the reaction medium (a dispersion of oil in a water/*t*-butanol/tetraethylammonium *p*-toluenesulfonate electrolyte) was either in the inward or outward radial direction. The innovative design of this reactor allows for a thin nickel bed and a high anode/cathode interfacial area without the normal problems associated with electrolyte flow distribution. The total size of the reactor can be increased without changing the relative anode/cathode position and the electrolyte flow pattern by simply increasing the length and/or number of anode/cathode elements in a single common shell (similar to a shell-and-tube heat exchanger). For the brush hydrogenation of soybean oil, current efficiencies of 90–100% were achieved with a single element reactor when the electrolyte oil content was 10 or 25 wt/vol %, the apparent current density was 10 or 15 mA cm^{-2}, the temperature was 75 °C, and the electrolyte flowed in the inward radial direction. The electrohydrogenated oil product was characterized by a high stearic acid content and low concentrations of linolenic acid and *trans* fatty acid isomers, as compared to the traditional high temperature chemical catalytic oil hydrogenation route with hydrogen gas.

1. Introduction

Numerous studies have shown that low hydrogen overpotential catalysts such as Raney nickel or platinum black can be used to hydrogenate electrocatalytically a variety of organic compounds including benzene and multiring aromatic compounds, phenol, ketones, nitro-compounds, dinitriles, and glucose [1–6]. In an electrocatalytic hydrogenation, atomic hydrogen is generated on an electrically conducting catalyst surface by the reduction of solvent molecules (e.g., water) from the adjacent electrolyte. The electrogenerated hydrogen then combines chemically with the organic reactant in solution. Electrocatalytic hydrogenation reactions have been carried out at moderate temperatures (<100 °C) and atmospheric pressure using both batch and semicontinuous flow reactors. In most cases the hydrogenated products were similar to those obtained from high temperature and pressure chemical catalytic reaction routes.

The hydrogenation of the fatty acid constituents of an edible oil's triglycerides, which is carried out to produce an oxidatively stable product and/or change a normally liquid oil into a semi-solid or solid fat, is a particularly attractive reaction to examine in an electrocatalytic scheme for the following reasons: (i) low reactor operating temperatures should minimize unwanted side reactions and the deleterious thermal degradation of the oil, (ii) normally, only 25–50% of the double bonds in an oil is hydrogenated, thus, eliminating the common problem of low hydrogenation current efficiencies when the unsaturated starting material is nearly depleted, and (iii) the high molecular weight of the starting oil (892 g mol^{-1} for refined soybean oil) means that the electrical energy consumption per pound of hydrogenated product will be low even though the saturation of a double bond requires 2 F mol^{-1}.

The triglycerides in refined soybean oil contain primarily 16 and 18 carbon fatty acids in the following distribution: 10.7 ± 1.2 wt % palmitic acid (16 carbons with no double bonds, which is normally abbreviated as C16:0), 3.9 ± 0.6 wt % stearic acid (C 18:0), 22.8 ± 2.7 wt % oleic acid (C 18:1), 50.8 ± 2.1 wt % linoleic acid (C 18:2), and 6.8 ± 1.6 wt % linolenic acid (C 18:3). The partial (brush) hydrogenation of soybean oil is practiced commercially to increase the oil's chemical stability (shelf life) by the selective reduction of the highly reactive linolenic fatty acids, without creating a solid or semi-solid fat via the production of large quantities of stearic acid (which has a melting point above room temperature). Most commercial hydrogenation plants use batch reactor equipment and Raney or supported nickel catalyst. The reaction

---

* To whom all correspondence should be sent.

0021-891X

Table 1. Chemical properties of the soybean oil starting materials

Starting oil	*Fatty acid profile*/wt %					*IV*	*% Free fatty acids**	*% Trans isomers*
	C 16:0	*C 18:0*	*C 18:1*	*C 18:2*	*C 18:3*			
Sunfresh	10.4	4.1	24.5	52.9	7.2	132	0.08	1.5
Lou Ana	10.5	3.8	22.6	54.0	8.8	136	0.05	3.0

* % Free fatty acids given as % oleic acid.

is carried out at a high temperature (typically 150–225 °C) and a hydrogen gas pressure between 10 and 60 psig (0.17–0.52 MPa) [7]. The hydrogenation rate and the oil's final fatty acid profile have been shown to depend on temperature, pressure, agitation rate in the reactor, and catalyst type and loading [8]. Unfortunately, the high reaction temperature needed for fast hydrogenation is known to produce a number of deleterious side reactions, including the production of cholesterol-forming *trans* fatty acid isomers [9,10].

Yusem and Pintauro [11] have shown that soybean oil can be hydrogenated electrochemically using Raney nickel powder as the catalytic cathode material. Constant current electrolyses were carried out at 70 °C with an undivided flow-through electrochemical reactor operating in a batch recycle mode. The reaction medium was a two-phase mixture of soybean oil in a water/*t*-butanol solvent containing tetraethylammonium *p*-toluenesulfonate as the supporting electrolyte. In all experiments the reaction was allowed to continue for sufficient time to synthesize a commercial-grade 'brush' hydrogenation product (25% theoretical conversion of double bonds). Hydrogenation current efficiencies in the range of 50–80% were obtained for apparent current densities of 10–20 mA cm^{-2} with an electrolyte oil concentration between 20 and 40 wt/vol %. A significant finding of this study was the low total *trans* isomer content of the electrochemically saturated oil product, which was in the range of 8–12%, as compared to the 20% *trans* product for a high temperature chemical catalytic brush hydrogenation process [12].

In the present paper, two new undivided radial flow-through Raney nickel powder reactors were built and tested for the electrocatalytic brush hydrogenation of soybean oil. The key (and common) component of the reactors is a cylindrical anode/cathode element with Raney nickel powder contained in the annular space between two concentric porous ceramic tubes. The design allows for a thin nickel bed and a high anode/cathode interfacial area without the normal problems associated with the flow distribution through the packed bed cathode. The total size of the reactor can be increased without changing the relative anode/cathode position and the electrolyte flow pattern by simply increasing the length and/or number of anode/cathode elements. Thus, scaleup of the reactor is conceptually simple, reactor size can be changed easily, and experimental data collected on a laboratory-size reactor can be used directly to model the performance of a large industrial unit.

2. Experimental details

2.1. *Materials*

Commercial grade Raney nickel powder (Degussa Corp., catalyst type BK111, supplied wet and in its active form) was used as the catalytic cathode material in all experiments. The reaction medium consisted of a dispersion of soybean oil in a mixture of reagent-grade *t*-butanol and deionized and distilled water. Tetraethylammonium *p*-toluenesulfonate (Sachem, Austin, TX), hereafter denoted as TEATS, was used as the supporting electrolyte. From a visual inspection of the two-phase reaction medium during an electrolysis, both TEATS and *t*-butanol appeared to improve the stability of the oil dispersion, probably by lowering the interfacial surface tension of the dispersed oil droplets. The TEATS salt played an additional role by providing quaternary ammonium ions which form an organic layer on the Raney nickel cathode surface; such a R_4N^+ film increased the affinity of the organic reactant (oil) with the catalyst which, in turn, improves the hydrogenation current efficiency [6,13]. Either a refined, bleached, and deodorized soybean oil from Sunfresh Inc. (St. Paul, MN) or a refined and bleached oil provided by Lou Ana Foods, Inc. (Opelousas, LA) was used in the electrolyses. Deodorization is a high temperature, vacuum steam stripping processing that is used to remove trace organic impurities from the oil (e.g., pigments and tocopherols). The deodorization process has no effect on the fatty acid profile of the oil's triglycerides, as evidenced by the similar C 16 and C 18 fatty acid compositions of the two starting oils in Table 1. Also listed in Table 1 are the Sunfresh and Lou Ana oils' free fatty acid and total *trans* isomer contents, which are essentially identical.

2.2. *Electrochemical reactors*

Soybean oil hydrogenation experiments were carried out using two undivided radial-flow reactors, which differed in the electrolyte flow direction (inward or outward flow). Schematic side cross-section diagrams of the reactors are shown in Figs 1 and 2. Each reactor contained a single anode/cathode element (5.6 cm dia.), with a Raney nickel catalyst bed contained in

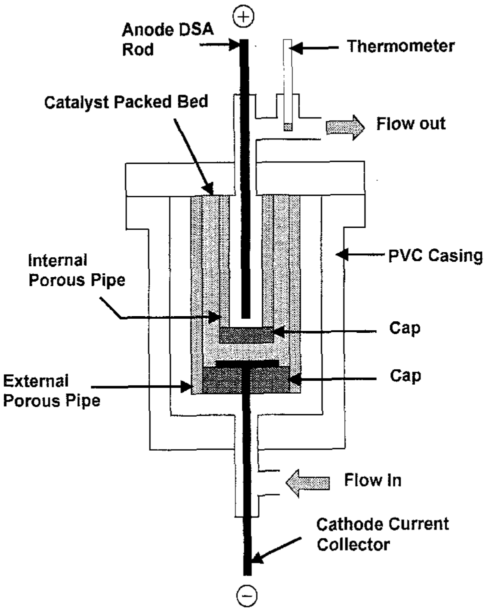

Fig. 1. Schematic side cross-section diagram of the inward-flow-direction reactor

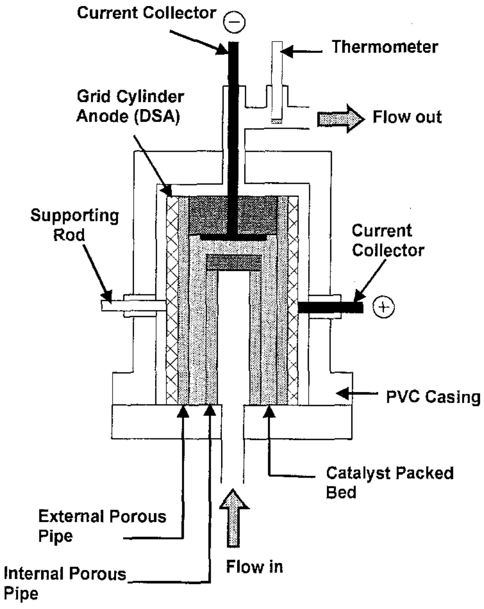

Fig. 2. Schematic side cross-section diagram of the outward-flow-direction reactor.

the annular space between two porous, ceramically bonded alumina tubes (Refractron Technologies Corp.). The catalyst bed was composed of approximately 80 g of Raney nickel powder and measured 6.55 cm (length) and 7.25 mm (thickness). A piston assembly was used to compress the powdered Raney nickel (to keep the catalyst in place as a compact bed) and also served as the electrical connector to the bed. For the inward-flow-direction reactor, a 1/4 in. DSA rod (Electrode Corp.) was placed in the open central chamber (with a diameter of 2.22 cm) which was formed by the inner porous tube. A DSA expanded grid (5.7 cm in diameter), positioned just beyond the outer porous cylinder, served as the anode in the outward-flow-direction reactor. A thermometer was placed in the outlet fitting of each reactor for measurement of the reaction temperature. A fine porosity ceramic tube (15 μm average pore size with a 5 mm wall thickness) was used to trap the Raney nickel powder (the inner tube for the inward-flow configuration and outer ceramic tube for the outward-flow-direction reactor), whereas the second tube for enclosing the nickel powder bed (5 mm tube wall thickness) had a larger average pore size (200 μm) to minimize flow resistance. The anode/cathode element was placed in a PVC plastic shell-casing (6.7 cm int. dia.). For the inward-flow-configuration cell, electrolyte entered the reactor through a single port at the bottom of the reactor and filled the gap formed by the shell casing and outer porous tube. The electrolyte passed first through the outer porous tube, then through the catalyst bed cathode, and finally through the inner ceramic tube. Electrolyte exited the reactor via a single outlet port connected to the central anode chamber. In the outward-flow direction reactor, electrolyte entered the anode/cathode element via the open central chamber and exited by way of the gap between the anode grid and outer PVC shell. In both reactor configurations, the anode was placed downstream from the cathode in order to eliminate current losses by a parasitic water oxidation/O_2 reduction redox couple. The radial flow patterns for both reactor configurations are shown in Fig. 3(a) and (b).

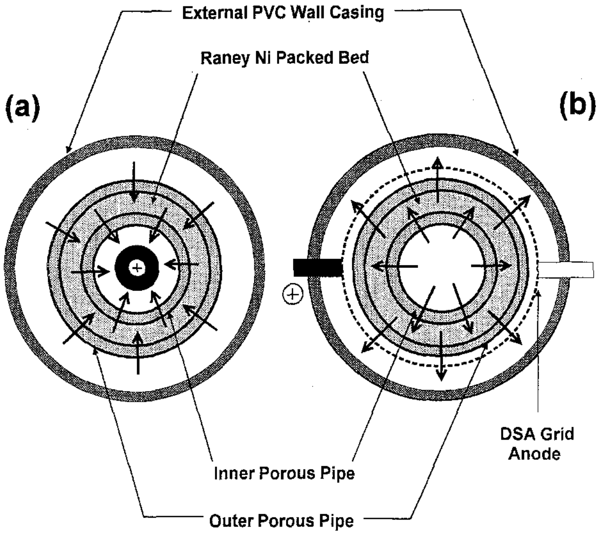

Fig. 3. Electrolyte flow patters for the radial flow-through reactors. (a) Inward-flow-direction reactor; (b) outward-flow-direction reactor.

For an oil hydrogenation experiment, the radial-flow reactor was placed in a batch recycle loop consisting of a high flow rate magnetic drive vane pump (Warrender Ltd, model MPA 114), a holding tank immersed in a constant temperature water bath, a flowmeter, and valves to control the liquid flow rate through the reactor. All experiments were performed with nitrogen gas purging the holding tank electrolyte, in order to remove dissolved electrogenerated oxygen and prevent its recirculation to the reactor. A magnetic stirrer in the holding tank provided sufficient agitation to maintain a dispersion of oil droplets in the water/*t*-butanol/TEATS electrolyte.

2.3. *Experimental procedures*

The catalyst was washed with soybean oil in the reactor prior to passing current, in order to remove trace amounts of hydrogen from the catalyst surface and, thus, insure that the hydrogenated oil detected at the conclusion of an electrolysis was produced by electrogenerated hydrogen. First, water was removed from the catalyst by circulating three 500 cm^3 aliquots of *t*-butanol through the batch recycle loop. Next, 400 cm^3 of a single-phase 50/50 wt % soybean oil/*t*-butanol solution at 70 °C was pumped through the reactor (under zero current conditions) for 12 h. The oil was emptied from the reactor/recycle loop apparatus and the catalyst was rinsed *in-situ* numerous times with 500 cm^3 portions of *t*-butanol, until no oil was detected in an alcohol washing.

In a typical oil hydrogenation experiment, 380 cm^3 of a water/*t*-butanol/TEATS solution containing a known weight of soybean oil (between 10 and 45 wt/vol %) was introduced into the reactor/recycle loop. The reaction mixture was pumped through the reactor at 300 $cm^3\,min^{-1}$. A constant direct current was applied for a specified period of time (depending on the weight of oil in the reaction medium and the applied current) in order to reduce theoretically ~25% of the double bonds in the initial oil (a total of 1054 coulombs was needed to fully saturate one gram of soybean oil). Apparent current densities (based on the anode/cathode interfacial area) in the range of 10–45 $mA\,cm^{-2}$ were employed, where the interfacial area for the inward-flow-direction and outward-flow-direction reactors was 64.8 cm^2 and 94.7 cm^2, respectively. Direct current to the reactor was provided by a Hewlett-Packard (6296A) power supply and monitored by a Keithley Instruments (model 169) digital multimeter. As a check against small current fluctuations over the course of an experiment, the total charge passed in an electrolysis was counted electronically using an Electrosynthesis Co. (model 640) digital coulometer.

At the conclusion of an experiment, the two-phase electrolyte was withdrawn from the reactor and the Raney nickel catalyst bed was washed several times *in situ* with 400 cm^3 volumes of *t*-butanol (each washing lasted 1 h). The electrolyte, oil, and butanol wash solutions were combined and the alcohol was removed under vacuum by rotary evaporation. An aqueous solution of Na_2SO_4 and 100 cm^3 of *n*-hexane were then combined with the oil/water/supporting electrolyte mixture in a separatory funnel. The top layer of hexane and oil was washed three times with water to remove all traces of TEATS salt. After vacuum evaporation of the n-hexane, the oil sample was analyzed for its chemical properties. Using this extraction procedure, 95–100% of the initial oil was recovered at the conclusion of an electrolysis.

2.4. *Product analysis*

The chemical characterization of the starting oil and hydrogenated product was performed in accordance with American Oil Chemists' Society (AOCS) procedures, as listed in 'Official Methods and Recommended Practices of the American Oil Chemists' Society' [14]. The fatty acid profile of initial and hydrogenated soybean oil samples was determined by gas chromatographic analysis of fatty acid methyl esters, according to AOCS methods Ce 2-66 and Ce 1-62. The esters were analysed using a Perkin-Elmer Sigma 115 gas chromatograph with a flame ionization detector and a glass-walled packed column (six feet in length) containing 3% SP-2310 and 2% SP-2300 on 100/120 Chromosorb WAW (Supelco, Inc. Bellefonte, PA). The GC was operated isothermally at 200 °C with injector and detector temperatures of 250 °C and a carrier gas of nitrogen (at a flow rate of 20 $cm^3\,min^{-1}$). Confirmation of fatty acid peaks was achieved by comparison with the retention times of authentic samples available commercially. The overall degree of oil hydrogenation is usually indicated by its iodine value (IV), which is expressed in terms of the number of centigrams of iodine absorbed per gram of oil (iodine reacts with the double bonds of unsaturated fatty acids). In the present study, the iodine value of oil samples was determined directly from the GC fatty acid composition (AOCS Method Cd 1c-85). The total isolated *trans*-isomer content of hydrogenated oil samples was determined by infrared spectrophotometry (Mattson Instruments FTIR, Madison, WI), as described by AOCS method Cd 14-61. The free fatty acid content of the oil (free fatty acids are formed by the base-catalyzed hydrolysis of the oil's triglycerides) was determined by base titration, in accordance with AOCS method Ca 5a-40.

3. Results and discussion

The current efficiency for soybean oil hydrogenation was calculated from the change in the total moles of double bonds in the oil (as determined from GC analyses of starting oil and final product samples) and the total charge passed in an electrolysis,

$$\text{Current efficiency }(\%) = 100(\Delta\text{ moles of double bonds})\,(2\text{ equiv}\,\text{mol}^{-1})F/Q \qquad (1)$$

where F is Faraday's constant and Q is the total charge passed in an experiment. The reaction selectivity for stearic acid formation and linolenic acid reduction was quantified in terms of the stearic selectivity, *SS*, (defined as the percentile increase in the oil's stearic acid content over the course of a hydrogenation per unit change in iodine value), and the linolenic selectivity, *LS*, (the percentile decrease in linolenic acid content between the starting oil and product per unit IV change). One additional selectivity index, the specific isomerization ratio (SI), was used to gauge the fatty acid *cis*-to-*trans* isomerization rate during an electrohydrogenation reaction, where SI is defined as the

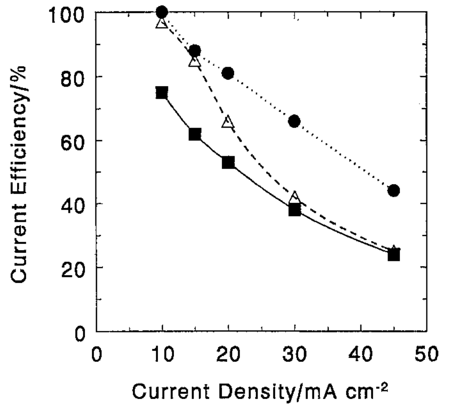

Fig. 4. Soybean oil hydrogenation current efficiency at different apparent current densities and electrolyte oil contents. Key: (●) 10 wt/vol % oil; (△) 25 wt/vol % oil; (■) 45 wt/vol % oil.

percent increase in total *trans* isomers content at the conclusion of a hydrogenation experiment per unit decrease in the oil's IV.

3.1. *Inward-flow-direction reactor studies*

The majority of the soybean oil electrolyses were performed with the inward-flow-direction reactor and the results of these experiments are presented first. Previous electrocatalytic hydrogenation studies (e.g., [2] and [6]) have shown that the organic reactant concentration, temperature, and applied current density are important operating parameters which influence significantly the reaction current efficiency. In the present study, an initial set of soybean oil hydrogenation experiments was performed at five different apparent current densities (10, 15, 20, 30 and 45 mA cm^{-2}) and three electrolyte oil contents (10, 25 and 45 wt/vol %). The reaction temperature was fixed at 75 °C, the solution flow rate was 300 cm^3 min^{-1}, and the solvent was composed of 50/50 vol % water/*t*-butanol containing 0.5 M TEATS as the supporting electrolyte. The current efficiency results of these fifteen experiments are shown in Fig. 4. As is normally the case, increasing the applied current density, for a given electrolyte oil content, resulted in a decrease in hydrogenation current efficiency. Current losses were attributed solely to hydrogen gas evolution. A decrease in current efficiency was also observed when the oil content in the electrolyte was increased (at a given current density). This result is opposite to that observed when the reactant is soluble in the solvent/supporting electrolyte mixture and suggests that there may have been oil droplet agglomeration in the cathode bed (which would restrict full access of the oil to the nickel surface) and/or deactivation of the nickel catalyst by an oil film (which would force hydrogen generation to occur on a smaller portion of the cathode bed) during the high oil content runs. The highest current efficiencies (in the range of 90%–100%) were achieved when the electrolyte oil content was either 10% or 25% and the current density was either 10 or 15 mA cm^{-2}.

Table 2 lists the chemical properties of the final oil product corresponding to the data points in Fig. 4. As the degree of hydrogenation increased (i.e., as the IV of the oil product decreased), the 18:2 and 18:3 content decreased and the 18:0 and 18:1 fatty acid concentrations increased (errors in the fatty acid composition of the oil products ranged from ±0.2 wt % for stearic acid to ±0.5 wt % for linolenic and linoleic acids). Also, the *trans* isomer content of the oil product increased with decreasing IV (errors in the *trans* isomers results in Table 2 were estimated to be plus or minus one percentage point). In general, we found that the stearic acid and linolenic acid selectivities were essentially constant and independent of

Table 2. Chemical properties of electrohydrogenated soybean oil for variations in electrolyte oil content and current density

Experimental conditions: Inward-flow-direction reactor; 300 cm^3 min^{-1} flow rate; 0.5 M TEATS supporting electrolyte; 75 °C reaction temperature; 50/50 vol % water/*t*-butanol solvent; Sunfresh soybean oil.

Exp.	*Oil content*; current density/* mA cm^{-2}	*Fatty acid profile/*wt %					*IV*	*% Trans isomers*	*Selectivity*			*% Free fatty acid*
		16:0	*18:0*	*18:1*	*18:2*	*18:3*			*SS*	*LS*	*SI*	
1	10%; 10	11.0	5.8	64.6	17.4	0.7	87	13.2	0.038	0.14	0.26	0.28
2	10%; 15	10.6	4.7	50.2	31.7	1.8	103	18.0	0.021	0.19	0.57	0.15
3	10%; 20	10.6	4.7	49.5	32.7	1.9	104	12.6	0.021	0.19	0.40	0.32
4	10%; 30	11.0	4.6	43.4	37.8	2.6	110	10.6	0.023	0.21	0.41	0.63
5	10%; 45	10.2	4.5	37.1	43.5	3.7	117	8.0	0.027	0.23	0.44	0.32
6	25%; 10	10.3	4.8	54.7	28.2	1.1	99	16.2	0.021	0.19	0.45	0.40
7	25%; 15	10.4	4.7	50.4	32.1	1.6	103	12.9	0.021	0.19	0.40	0.39
8	25%; 20	10.4	4.5	44.3	37.6	2.3	109	5.4	0.017	0.21	0.17	0.57
9	25%; 30	10.4	4.4	37.1	43.4	3.9	117	8.2	0.020	0.22	0.45	0.66
10	25%; 45	10.2	4.6	31.9	47.4	5.0	123	8.8	0.056	0.24	0.82	1.64
11	45%; 10	10.2	4.7	47.2	35.3	1.9	107	11.1	0.024	0.21	0.39	0.32
12	45%; 15	10.5	4.8	42.1	39.0	2.8	111	11.5	0.033	0.21	0.48	0.78
13	45%; 20	10.0	4.4	41.9	40.5	2.8	114	10.9	0.017	0.24	0.52	0.25
14	45%; 30	10.5	5.2	41.4	39.2	2.8	111	11.0	0.052	0.21	0.45	1.44
15	45%; 45	10.5	4.2	31.7	47.5	5.1	123	4.7	0.011	0.23	0.36	0.24

* Oil content given as wt/vol %.

Table 3. Effect of temperature on current efficiency and product composition for the electrocatalytic hydrogenation of soybean oil

Experimental conditions: Inward-flow-direction reactor; 10 mA cm^{-2} current density; 1.0 M TEATS supporting electrolyte; 300 cm^3 min^{-1} flow rate; 50/50 vol % water/*t*-butanol solvent containing 25 wt/vol % sunfresh soybean oil.

Reaction temperature/°C	*Fatty acid profile*/wt %				*IV*	*Current efficiency* /%	*% Free fatty acid*	*% Trans isomers*
	18:0	*18:1*	*18:2*	*18:3*				
45	4.3	27.3	52.0	5.4	128	12	0.38	6.2
60	4.5	46.3	36.2	2.0	108	72	0.36	13.0
70	5.4	46.6	35.2	1.7	111	78	0.46	12.3

electrolyte oil content and applied current and somewhat higher than those reported for a high temperature chemical catalytic brush hydrogenation with Raney nickel catalyst (where $SS = 0.018$ and $LS = 0.173$ [12]). The low percentage of free fatty acids (averaging 0.55%) indicates that there is good mixing of the alkaline solution in the nickel bed with the low pH electrolyte in the anode chamber. The average SI (*trans* isomer selectivity) for the 15 experiments in Table 2 is 0.438, as compared to 0.81 for a chemical catalytic hydrogenation process [12]. The lower *trans* isomer content in the oil is attributed to the lower operating temperature of the reactor (75 °C vs 150–225 °C). Recent studies have indicated that diets high in *trans* isomer fats and oils raise the blood levels of harmful low density lipoprotein cholesterol [15] and in this regard the electro-hydrogenated oil product is more desirable than that from a conventional chemical catalytic process.

The effect of reaction temperature (45, 60 and 70 °C) on the hydrogenation current efficiency and the chemical composition of the soybean oil product is shown in Table 3. A dramatic increase in current efficiency was observed when the reaction temperature was increased from 45 °C (12% current efficiency) to 60 °C (72% current efficiency). When the reaction temperature was further increased to 70 °C, the current efficiency showed only a modest improvement (to 78%). The rate of hydrogen generation on the nickel surface during constant current reactor operation is independent of temperature but the consumption of hydrogen via its chemical reaction with oil increases with increasing temperature [8]. A high solution temperature, thus, lowers the catalyst surface concentration of H and decreases the rate of unwanted hydrogen gas evolution. These results are consistent with prior electrocatalytic organic hydrogenation studies (e.g., [6]). The percentage of free fatty acids at the conclusion of an electrolysis was found to be low and independent of reaction temperature, again indicating a uniform flow of electrolyte from the cathode bed to the anode chamber, which minimizes stagnant oil pockets inside the Raney nickel bed (where oil is in contact with high pH aqueous electrolyte). The 45 °C experiment showed the lowest *trans* isomer content, although it exhibited the highest SI value (a high degree of *trans* isomer formation per unit change in IV) due to the low hydrogenation current efficiency and small decrease in IV. The 70 °C experiment showed the lowest SI selectivity. The decreasing trend in SI selectivity with increasing temperature for the electrocatalytic reaction scheme is opposite to that reported in the literature for the chemical catalytic oil hydrogenation process, which is normally carried out at much higher temperatures [12,16,17]. In the electrochemical process, it appears that a decrease in temperature slows the rate of oil hydrogenation to a greater extent than the *cis-trans* isomerization reaction.

The effect of TEATS supporting electrolyte concentration (in the range of 0.5–2.0 M) on the current efficiency and product yield during soybean oil hydrogenation is shown in Table 4. The low current efficiencies for TEATS concentrations of 1.5 and 2.0 M are attributed to the high solution viscosity which lowers the mass transfer coefficient at the nickel surface for a given fluid velocity and impedes contact of the oil droplets with the catalyst surface. This point is further demonstrated by the high stearic acid content of the 1.5 and 2.0 M TEATS experiments. There appears to be insufficient fluid velocity near the catalyst surface (due to viscous

Table 4. Effect of TEATS supporting electrolyte concentration on the performance of the soybean oil electrohydrogenation reaction

Experimental conditions: Inward-flow-direction reactor; 75 °C reaction temperature; 10 mA cm^{-2} current density; 300 cm^3 min^{-1} flow rate; 50/50 vol % water/*t*-butanol solvent containing 20 wt/vol % Sunfresh soybean oil.

Supporting electrolyte	*Fatty acid profile*/wt %					*IV*	*Current efficiency*/%
	16:0	*18:0*	*18:1*	*18:2*	*18:3*		
0.5 M TEATS	10.3	4.6	46.5	35.9	2.0	107	72
1.0 M TEATS	10.3	5.4	46.6	35.2	1.7	105	78
1.5 M TEATS	10.5	7.5	38.0	40.1	2.9	110	64
2.0 M TEATS	10.9	6.6	40.5	38.8	2.5	109	63

Table 5. Performance of the outward-flow-direction reactor

Experimental conditions: 70 °C reaction temperature; 300 cm^3 min^{-1} flow rate; 10 wt/vol % Lou Ana soybean oil.

Solvent/supporting electrolyte	*Current density* /mA cm^{-2}	*Fatty acid profile*/wt %					*IV*	*% Free fatty acids*	*% Trans isomers*	*Current efficiency*/%
		16:0	*18:0*	*18:1*	*18:2*	*18:3*				
Water/1.0 M TEATS	13.7	10.6	5.6	40.4	38.8	4.1	113	0.61	12.7	69
50/50 vol % water/*t*-butanol/ 0.5 M TEATS	13.7	10.5	4.9	40.3	40.2	3.8	114	0.62	24.9	64
Water/1.0 M TEATS	20.6	10.4	4.9	41.5	39.2	3.8	113	0.37	17.5	66
50/50 vol % water/*t*-butanol 0.5 M TEATS	20.6	10.4	4.2	40.1	41.4	3.7	116	0.55	12.0	59

drag effects) to dislodge adhered oil droplets, in which case the oil remains on the catalyst surface for a sufficient length of time for complete hydrogenation of all triglyceride double bonds.

3.2. *Outward-flow-direction reactor studies*

Four soybean oil electrolysis experiments were performed with the outward-direction radial flow reactor. The reaction medium contained 10 wt/vol % soybean oil dispersed in either pure water (with 1.0 M TEATS supporting electrolyte) or a 50/50 vol % water/*t*-butanol solvent with 0.5 M TEATS. The solution flow rate (300 cm^3 min^{-1}) was identical to that used in the inward-direction flow reactor. The apparent current density was either 13.7 or 20.6 mA cm^{-2} and sufficient charge was passed in an electrolysis to hydrogenate theoretically 25% of the double bonds in the starting oil. The results of these hydrogenation experiments, in terms of the reaction current efficiency, final fatty acid product distribution, % free fatty acids, and final percentage of total *trans* isomers are listed in Table 5.

The current efficiency for soybean oil hydrogenation ranged from 59–69%, as compared to 81–88% for the inward-flow-direction reactor under similar operating conditions (see Fig. 4). The lower current efficiencies in Table 5 may have been due to either: (i) the difference in purity of the Sunfresh and Lou Ana starting oils (only the former was deodorized), in which case trace impurities in the oil partially poisoned the catalyst (deactivated oil hydrogenation sites) and promoted hydrogen evolution and/or (ii) poor flow distribution through the nickel bed which led to a deterioration in the oil/electrolyte dispersion. Although the flow rate of 300 cm^3 min^{-1} was the same for the two flow configuration reactors, the linear velocity of the oil dispersion in that portion of the Raney nickel bed closest to the anode, where most of the hydrogen is generated (the inner surface of the annular bed for the inward-direction reactor or the outer bed surface for the outward-configuration flow reactor), was lower for the outward direction reactor. This second hypothesis is as yet unproven (higher flow rate experiments were not performed with the outward-flow-configuration reactor in the present study), but low oil dispersion flow rates through a Raney nickel catalyst cathode bed have been shown to decrease the current efficiency for soybean oil hydrogenation [13].

Based on the limited number of experiments in Table 5, there is no significant drawback in terms of current efficiency when *t*-butanol co-solvent is removed from the reaction medium. The relative change in the fatty acid profile of the oil products in Table 5, as well as the percentage of free fatty acids, are comparable to those in Table 2 for the inward-flow-direction reactor. The percentage *trans* isomers in the outward-flow-direction reactor are somewhat higher than those listed in Table 2, but further outward-flow experiments are needed before any definitive conclusion can be made. A significantly lower anode/cathode voltage drop, however, was measured with the outward-flow-direction reactor (6–8 V for run 4 in Table 5 vs 18–19 V for the inward-flow reactor at a similar current density). The lower operating voltage for the outward-direction flow cell (which translates into a lower electrical energy requirement per kilogram of oil product) was not surprising, since the distance between the Raney nickel bed and DSA grid in this reactor was smaller than that in the inward-flow reactor. It is obvious from these results that the DSA rod in the inward-flow-direction reactor should be replaced by a DSA grid that is pressed up against the inside surface of the inner porous ceramic tube. Further decreases in cell voltage could be made for both the inward and outward-direction flow cells by reducing the thickness of the porous ceramic tube that separates the anode and cathode bed, but experiments with such a reactor were not performed in the present study.

3.3. *Scale-up considerations*

An attractive aspect of the radial-flow reactor configuration (either inward- or outward-flow direction) is the simplicity of scaling a laboratory reactor to pilot or full commercial size. The industrial scale-up configuration of a radial-flow reactor would be similar to that of a shell-and-tube heat exchanger, where the required number of anode/cathode elements are the inner tubes that are contained in a single common shell. For anode/cathode inward-flow direction elements, a single feed solution is supplied to the shell-side of the

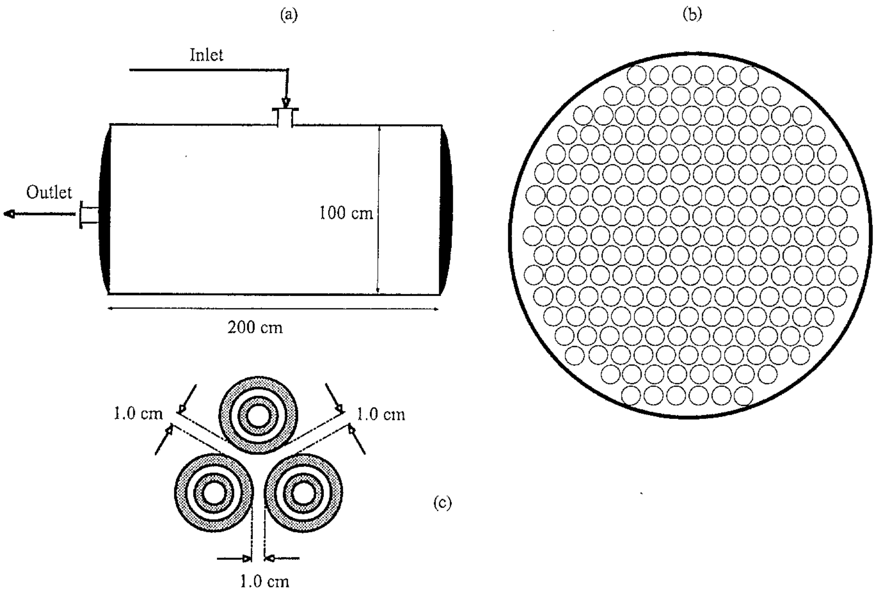

Fig. 5. Design of a commercial-size electrocatalytic hydrogenation reactor employing 200 inward-flow-direction anode/cathode elements. (a) Overall shell dimensions; (b) cross-sectional view showing 200 tubes; (c) triangular arrangement of the anode/cathode elements.

reactor and product exits through the central anode chambers of each reactor element. With this reactor configuration, difficulties normally encountered in reactor scale-up and design [18–20] are circumvented because the surface area of the catalytic cathode can be enlarged without altering the relative anode/cathode position and the electrolyte flow pattern through each tubular electrode element. By placing many tubular anode/cathode elements into a common reactor shell, thereby increasing the total anode/cathode interfacial area per unit reactor volume, high reactor space–time yields can be achieved for a low current density electrocatalytic hydrogenation reaction.

An example of a hypothetical commercial-size, multiple anode/cathode element electrocatalytic hydrogenation reactor is shown in Fig. 5(a)–(c). The reactor contains 200 anode/cathode tubular elements, each 200 cm in length. Each anode/cathode element has the same radial dimensions as the inward-flow direction reactor used in the laboratory-scale soybean oil hydrogenation experiments described above. The positioning of both the tubes and the casing surrounding the electrode bundle was designed to minimize void volume inside the shell. The tube assemblies were positioned in a triangular arrangement, with a 1.0 cm gap between tubes. This electrode layout required an outer shell 100 cm in diameter (see Fig. 5(b) and (c)). The total anode/cathode interfacial area for each 200 cm long tube is 1979 cm^2 and the total interfacial area for a 200 tube reactor is 395 841 cm^2. A single feed port is used to introduce the feed solution into the reactor and the exit port from each anode discharges the oil/electrolyte dispersion into a common header. If such a reactor were employed to partially hydrogenate soybean oil from an IV of 135 to an IV of 108 (i.e., a 20% reduction in the number of double bonds) at operating conditions identical to those used in laboratory experiments (i.e., a reaction medium of 10 wt/vol % oil dispersed in 50/50 vol % water/*t*-butanol with a current density of 20 mA cm^{-2} and a current efficiency of 80%, as listed in Table 2 and Fig. 4), then the annual oil output from such a reactor would be 8.93×10^5 kg [13].

4. Conclusions

A novel undivided radial-flow-through electrochemical reactor for the partial (brush) hydrogenation of soybean oil was designed, constructed, and tested. The unique features of this reactor are: (i) a tubular element anode/cathode design, where Raney nickel catalyst powder is packed in the annual space between two concentric porous ceramic tubes and (ii) the electrolyte flow pattern, which is in the radial direction to minimize flow resistance and insure a uniform flow distribution through the entire packed bed. Two prototype reactors were tested in the present study, with the flow of solution in either the inward or outward radial direction. The reaction medium consisted of a two-phase dispersion of soybean oil in a solution of water or a water/*t*-butanol mixture, with a quaternary ammonium salt as the supporting electrolyte. For the inward-flow direction reactor, hydrogenation current efficiencies of 90–100% were achieved when the electrolyte oil content was either 10 or 25 wt/vol % and the apparent current density was either 10 or 15 mA cm^{-2}. The oil product was characterized by a higher stearic acid content and lower concentrations of linolenic acid and *trans* fatty acid isomers, as compared to the traditional high temperature chemical catalytic oil hydrogenation route with hydrogen gas. Performance data from laboratory-size radial-flow reactors can be used directly during scale-up calculations for pilot or commercial size cells. Such large reactors have a conceptually simple design, with many tubular anode/cathode elements in a common housing (resembling a shell-and-tube heat exchanger). In contrast to other flow-through electrochemical reactors, the total apparent anode/cathode area (and rates of hydroproduct formation) can be increased, in principle, without changing either the geometric dimensions of the individual anode/cathode elements or the electrolyte flow pattern by simply increasing the number and/or length of the tubular electrode elements in a reactor.

Acknowledgement

This work was supported by the Cooperative State Research Service, US Department of Agriculture, under Agreement No. 94-37500-0634, the US Department of Energy, Advanced Industrial Concepts Division, through National Renewable Energy Laboratory subcontracts XD-10103-1 and XAE-4-14099-10, and by the Louisiana Educational Quality Support Fund, grant RD-B-14.

References

[1] T. Chiba, M. Okimoto, H. Nagai and T. Takata, *Bull. Chem. Soc. Jpn.* **56** (1983) 719.

[2] K. Park, P. N. Pintauro, M. M. Baizer and K. Nobe, *J. Electrochem. Soc.* **132** (1985) 1850.

[3] A. Cyr, P. Huot, G. Belot and J. Lessard, *Electrochim. Acta* **35** (1990) 147.

[4] D. Robin, M. Comtois, A. Martel, R. Lemieux, A. K. Cheong, G. Belot and J. Lessard, *Can. J. Chem.* **68** (1990) 1218.

[5] D. V. Sokol'skii, *Period. Polytech. Chem. Eng.* **27** (1983) 45.

[6] P. N. Pintauro and J. R. Bontha, *J. Appl. Electrochem.* **21** (1991) 799.

[7] R. J. Grau, A. E. Cassano and M. A. Baltanás, *Catal. Rev. Sci. Eng.* **30** (1988) 1.

[8] J. W. E. Coenen, *J. Am. Oil Chem. Soc.* **53** (1976) 382.

[9] H. W. B. Patterson, *Olégineux* **28** (1973) 583.

[10] R. P. Mensink and M. B. Katan, *New Engl. J. Med.* **323** (1990) 439.

[11] G. Yusem and P. N. Pintauro, *J. Am. Oil Chem. Soc.* **69** (1992) 399.

[12] R. C. Hastert, *J. Am. Oil Chem. Soc.* **58** (1981) 169.

[13] G. Yusem, PhD dissertation, Tulane University, New Orleans, LA (1994).

[14] 'Official and Recommended Practices of the American Oil Chemists' Society', 4th edn (edited by D. Firestone), American Oil Chemists' Society, Champaign, IL (1989).

[15] R. P. Mensink and M. B. Katan, *N. Engl. J. Med.* **323** (1990) 439.

[16] L. F. Albright, 'Hydrogenation: Proceedings of an AOCS Colloquium', (edited by R. C. Hastert), American Oil Chemists' Society, Champaign, IL (1986) pp. 11–29.

[17] R. R. Allen, *J. Am. Oil Chem. Soc.* **58** (1981) 166.

[18] D. E. Danly, *AIChE Symp. Ser. 204*, (edited by R. Alkire and T. Beck), **77** (1981) 39.

[19] J. R. Selman, *AIChE Symp. Ser 229* (edited by R. Alkire and D.-T. Chin), **79** (1983) 101.

[20] R. E. W. Jansson, *AIChE Symp. Ser 229* (edited by R. Alkire and D.-T. Chin), **79** (1983) 92.