

# Computer-aided electrochemical process design: simulation and economic analysis of an electrocatalytic soybean oil hydrogenation plant

G. YUSEM\*, P. N. PINTAURO‡

*Department of Chemical Engineering, Tulane University, New Orleans, LA 70118 USA*

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The process flowsheet for a soybean oil electrohydrogenation plant has been devised and heat and mass balance calculations on unit operations equipment were performed using a commercially available process simulation software package (PRO/II from Simulation Sciences, Inc.). The design and anticipated performance (current efficiency and power requirements) of the electrochemical flow cells were based on a laboratory-scale radial-flow-through Raney nickel powder electrocatalytic hydrogenation reactor. A semiempirical porous electrode model, that reproduced laboratory-scale reactor data, was incorporated into the PRO/II software as a unit operations subroutine module. Operation of a  $3.0 \times 10^6 \text{ kg y}^{-1}$  electrochemical plant was simulated on a computer for different soybean oil/electrolyte feeds and reactor current densities. Based on the PRO/II results, an economic analysis of the process, including capital, installation and operating costs of all equipment was carried out. The lowest total production cost for a brush hydrogenation oil product (20% reduction in the number of double bonds) was obtained at a current density of  $15 \text{ mA cm}^{-2}$  and a feed composition of 10 wt:vol % soybean oil in solvent/supporting electrolyte (US\$  $0.13 \text{ kg}^{-1}$  for an assumed five year straight line depreciation of capital equipment). This cost was higher than that for a comparable-size chemical catalytic soybean oil hydrogenation plant (US\$  $0.019 \text{ kg}^{-1}$ ). When the cost of the soybean oil starting material (US\$  $0.68 \text{ kg}^{-1}$ ) was factored into the economic analysis, the production plus raw material cost of the electrocatalytic process was only 16% greater than that for the chemical catalytic plant. The production cost for the electrosynthesized hydro-oil product may be tolerable because the oil has a high nutritional value (a lower *trans* isomers content) which may command a higher selling price.

Keywords: *Electrocatalytic hydrogenation, Porous electrode model, Raney nickel, Soybean oil, Process design*

## List of symbols

$a$	specific catalyst surface area per unit volume ( $\text{cm}^{-1}$ )	$\hat{j}_1, \hat{j}_2, \hat{j}_3$	average reaction rates in the catalytic cathode bed associated with Equations 1, 2 and 3 ( $\text{gmol cm}^{-2} \text{ s}^{-1}$ )
$C_{\text{oil}}$	concentration of oil in the reaction medium (wt:vol %)	$K_1, K_2, K_3$	empirical constants that appear in Equations 9 and 10
$F$	Faraday's constant ( $96\,487 \text{ C equiv}^{-1}$ )	$n_{\text{db}}$	number of double bonds reduced in one mole of soybean oil
$i$	current density ( $\text{A cm}^{-2}$ )	$r$	radial position (cm)
$i_{\text{app}}$	constant applied current density ( $\text{A cm}^{-2}$ )	$R$	gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
$i_{\text{o},1}$	exchange current density for the Volmer reaction, Equation 1 ( $\text{A cm}^{-2}$ )	$T$	temperature (K)
$j_1, j_2, j_3$	local reaction rates within the catalytic cathode bed associated with Equations 1, 2 and 3, respectively ( $\text{gmol cm}^{-2} \text{ s}^{-1}$ )	<i>Greek symbols</i>	
		$\alpha$	charge transfer coefficient
		$\eta$	activation overpotential (V)
		$\kappa$	electrolyte conductivity ( $\Omega^{-1} \text{ cm}^{-1}$ )

## 1. Introduction

Commercially available heat and mass transfer computer simulation programs are used on a regular

basis in the chemical and petrochemical industries for preliminary plant design and process optimization calculations and to assist engineers in anticipating the performance of unit operations equipment. The use

\* Present address: Tektronix, Inc., Wilsonville, Oregon 97070, USA. ‡ Author to whom correspondence should be addressed.

of these software packages for organic electrochemical processes has received much less attention because of the difficulty in computing thermodynamic properties of nonideal electrolytic solutions and because the reactor modules in these programs can not accommodate the unique current/voltage operating criteria of electrochemical cells and the kinetic rate expressions for electrochemical reactions. Although there have been improvements in the ability of simulators to predict thermodynamic properties of electrolytes, built-in sophisticated electrochemical reactor models are nonexistent. One can argue that electrochemical reaction routes would be considered more often as alternatives to chemical catalytic schemes if engineers could perform preliminary heat and mass balance and scale-up analyses on organic electrochemical processes. Such calculations would be used to evaluate and optimize the interrelationship between process economics (e.g., the cost and complexity of product purification equipment downstream from the reactor) and the current/voltage distribution, kinetic, and mass transfer events that regulate product and byproduct reactions in an electrochemical reactor.

A limited number of computer-generated heat and mass balance simulations of electroorganic processes have been reported in the literature [1–4]. The focus of these investigations was to use commercially available process design software packages to model rigorously the unit operations equipment upstream and downstream from the electrochemical reactor. The electrochemical cells, however, were modelled as standard chemical reactors that were operated at a fixed conversion of feed material. To date, there is no published computer-aided process design study where the electroorganic reactor model is integrated completely within the simulation software and where reactor performance is described in terms of complex kinetic rate expressions or a sophisticated porous electrode model.

In the present paper, a process design and simulation computer code for the electrocatalytic hydrogenation of soybean oil was developed and then used to perform an overall assessment of plant economics. This is the first reported work where the Fortran computer code for the prediction of a packed bed reactor's current/voltage distribution and current efficiency for organic synthesis is coupled to the heat and mass balance computer modules for other unit operations. The configuration and operation of the electrochemical reactors in the proposed soybean oil hydrogenation plant were based on a laboratory-scale radial-flow Raney nickel powder reactor that is described in detail elsewhere [5]. A semiempirical porous electrode computer model, which reproduced laboratory-scale reactor current efficiency data, was linked to a commercially available heat and mass balance software package (PRO/II software sold by Simulation Sciences, Inc., Fullerton, CA). The electrochemical plant was simulated for different soybean oil/electrolyte feed compositions and different reactor

current densities. An economic analysis of the process, including capital and operating costs of all unit operations equipment in the hydrogenation plant, was carried out to determine the reactor operating conditions that minimized the total cost per pound of product.

### 1.1. Background: electrocatalytic hydrogenation of soybean oil

The partial hydrogenation of the fatty acid constituents of an edible oil's triglycerides is carried out to produce an oxidatively stable product and/or to convert a liquid oil into a solid or semisolid fat. During the partial (brush) hydrogenation of soybean oil, the goal is to lower the concentration of 18-carbon triene fatty acids without increasing substantially the concentration of stearic acid (the 18-carbon, fully saturated fatty acid). In the electrocatalytic hydrogenation of soybean oil, atomic hydrogen is formed electrochemically on a catalytically active Raney nickel cathode surface by the discharge of water or protons from the adjacent solution. The absorbed hydrogen then reacts chemically with the oil substrate. Prior studies by the present authors [5,6] have shown that soybean oil can be partially electrohydrogenated at atmospheric pressure, a constant current density between 10 to 45 mA cm<sup>-2</sup> and a moderate temperature using laboratory-scale axial and radial-flow undivided cells containing a Raney nickel powder cathode. In these studies, a two-phase reaction medium was employed, where soybean oil was dispersed in a water/*t*-butanol solvent with tetraethylammonium *p*-toluenesulfonate (TEATS) as the supporting electrolyte. Oil hydrogenation current efficiencies were high and the oil product was characterized by a minimum increase in the concentration of stearic acid and a *trans* fatty acid isomers concentration lower than that found in a chemically hydrogenated oil product (the ingestion of *trans* isomers was reported to have deleterious health effects by raising blood levels of cholesterol [7].) In the radial flow-through reactor, an oil dispersion was pumped in the inward radial direction through a thin packed bed of Raney nickel catalyst that was contained within the annular space between two concentric porous ceramic tubes. After passing through the cathode, the reaction mixture entered a central anode chamber, where the water component of the electrolyte was oxidized to O<sub>2</sub> at a DSA rod before exiting the reactor. This flow cell design (shown schematically in Fig. 1 of [5]) is particularly well suited to scale-up calculations because the total apparent anode/cathode area (which is directly proportional to the rate of hydroproduct formation) can be increased, in principle, without changing either the geometric dimensions of individual tubular anode/cathode elements or the electrolyte flow pattern through the packed bed cathode [5]. Due to the low operating current density of the laboratory-scale flow cell, however, an industrial size reactor with high space-

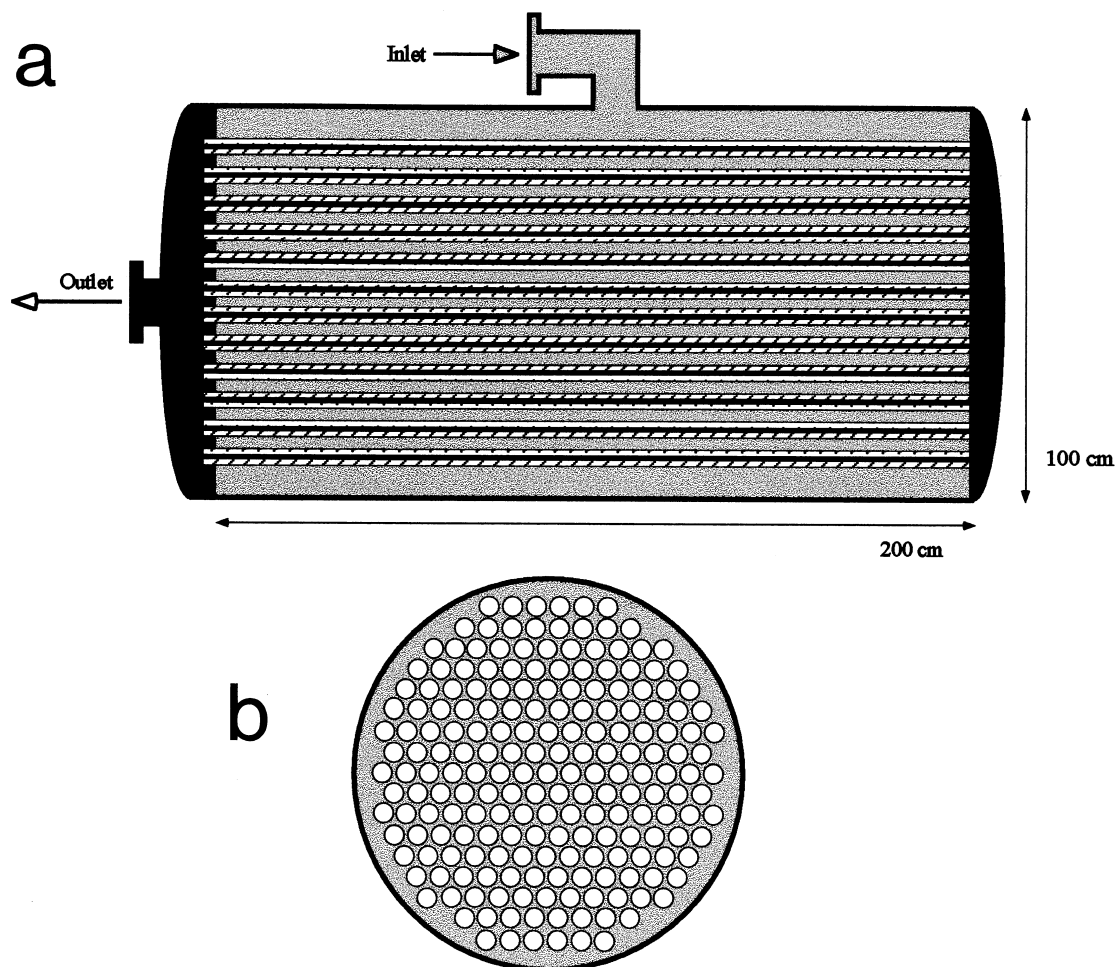


Fig. 1. Schematic cross-section diagrams of a hypothetical industrial-size radial-flow electrocatalytic hydrogenation reactor containing multiple anode/cathode tubular elements. (a) Side cross-section view showing the overall dimensions of the reactor; (b) end cross-section view showing the placement of 200 tubular elements.

time yields would require 200 or more tubular anode/cathode elements contained in a common shell (the design would be similar to a shell-and-tube heat exchanger). Side and end view schematic diagrams of such a multielement reactor are shown in Fig. 1.

Current efficiencies for the brush hydrogenation of soybean oil in the laboratory-size radial-flow electrocatalytic reactor at 75 °C ranged from 24% to 100% and were found to increase with decreasing current density and decreasing concentration of oil in the two-phase reaction medium [5]. Hydrogenation current efficiencies less than 100% were due to hydrogen gas evolution; there were no side reactions that generated oil byproducts. This reactor performance data has been used in the present study to both model the electrocatalytic flow reactor and to evaluate the effects of current density and oil/electrolyte composition on the economics of a soybean oil electrohydrogenation plant.

## 2. Process flow sheet

The electrocatalytic hydrogenation plant was sized for an annual production  $2.95 \times 10^6$  kg  $y^{-1}$  of partially hydrogenated soybean oil (where the number of double bonds in the starting oil was reduced by 20%).

The analysis was based on 342 net working days per year, which corresponds to a continuous hydrogenation rate of 100 g  $s^{-1}$  or 360 kg  $h^{-1}$ . A flow sheet for the proposed electrocatalytic hydrogenation process is shown in Fig. 2 and process specifications for the different unit operations equipment in the design are listed in Table 1. The plant operates with a continuous feed of fresh soybean oil (stream 1) and produces a continuous output of partially hydrogenated soybean oil product (stream 17). The process also has a continuous input of pure water (stream WM) to compensate for water consumed in the anodic and cathodic electrochemical reactions and a continuous purge of electrochemically generated  $H_2$  and  $O_2$  gases (stream 31). The electrochemical reactor loop in Fig. 2 consists of: (i) a mixing tank MIX1 (where the two-phase feed to the reactor is generated), (ii) the electrochemical reactor system ERS, and (iii) splitter SPT, which regulates the fraction of oil/electrolyte to be sent to the separation/purification loop vs that which is recycled back to the reactors.

The electrochemical reactor system, ERS, shown as a single block in Fig. 2, is comprised of a set of identical multiple element radial-flow reactor units. Figure 3 depicts the arrangement of a hypothetical ERS involving four reactor units, operated in series,

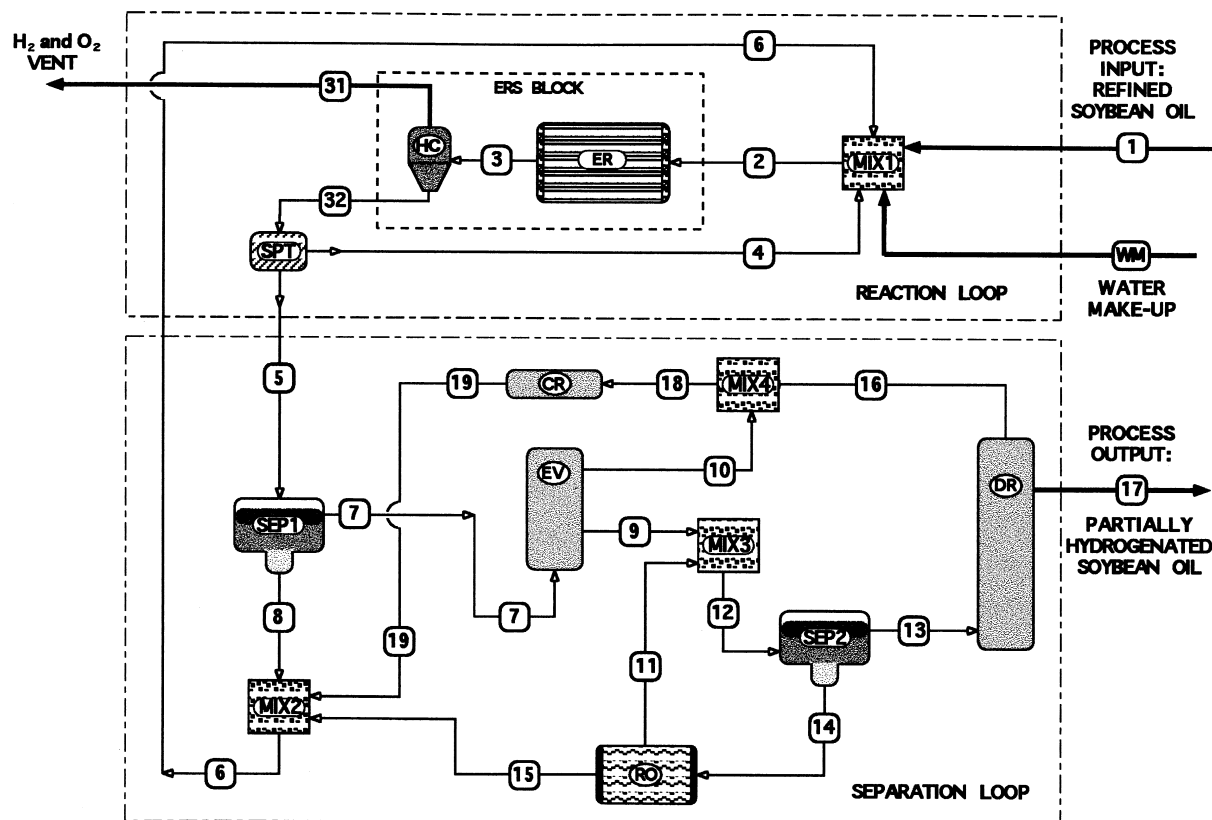


Fig. 2. Process flowsheet for the soybean oil electrocatalytic hydrogenation plant.

where the electrolyte leaving the last reactor unit constitutes the ERS output stream (stream 32 in Fig. 2). The actual number of reactors in a given plant would depend on the production level of hydro-oil, the operating current density, and the current efficiency for hydrogenation. Each reactor unit in Fig. 3 includes: (i) one pump, (ii) one water-cooled static mixer, (iii) one electrocatalytic multielement radial-flow cell and (iv) one hydrocyclone. The

function of the static mixers is to provide an emulsified two-phase electrolyte feed to each reactor and to maintain a constant feed temperature for all reactor units by removing the heat generated in the preceding reactor (i.e., the exothermic heat of reaction during oil hydrogenation and ohmic heating of the electrolyte). Each hydrocyclone insures that electrogenerated  $O_2$  gas formed in one reactor will not be carried over to the next (which would lower

Table 1. Process specifications for the electrocatalytic hydrogenation of soybean oil

Name	Unit operation	Process specifications*†
MIX1	Mixing tank	70 °C stream 2.
ER	Electrochemical reactor	20% conversion in stream 3. Heat generated in reactor was removed to maintain reaction at constant temperature (70 °C).
HC	Hydrocyclone	Isothermal operation. No gases in stream 32 and no water, oil, or <i>t</i> -butanol in stream 31.
SPT	Splitter	Isothermal operation. Total oil content in stream 5 was set equal to that of stream 1.
SEP1	Phase separator	Isothermal operation. Residence time: 1 h. Separation factors for stream 7: oil, 100%; <i>t</i> -butanol, 50%; water, 5%; TEATS, 1%.
EV	Evaporator	Vapour temperature: 85 °C. Liquid temperature: 83 °C. Separation factors for stream 9: oil, 100%; <i>t</i> -butanol, 1%; water, 99%; TEATS, 100%.
CR	Condenser	70 °C in stream 19.
MIX2	Mixing tank	70 °C in stream 6.
MIX3	Mixing tank	Adiabatic. Ratio of water to oil in stream 12 was set equal to 3.
MIX4	Mixing tank	Adiabatic.
SEP2	Phase separator	Isothermal operation. Residence time: 1 h. Separation factors for stream 13: oil, 100%; <i>t</i> -butanol, 100%; water, 0.5%; TEATS, 0%.
RO	Reverse osmosis	Separation factors for stream 11: pure water at constant mass flow rate.
DR	Dryer	Vapour temperature: 120 °C. Liquid temperature: 120 °C. Separation factors for stream 17: oil, 100%; <i>t</i> -butanol, 0%; water, 0%; TEATS, 0%.

\* Separation factor for each component was calculated as a mass percentage of that component in the corresponding feed.

† The term 'Oil' refers to the total soybean oil in a stream (i.e., partially hydrogenated and unreacted soybean oil).

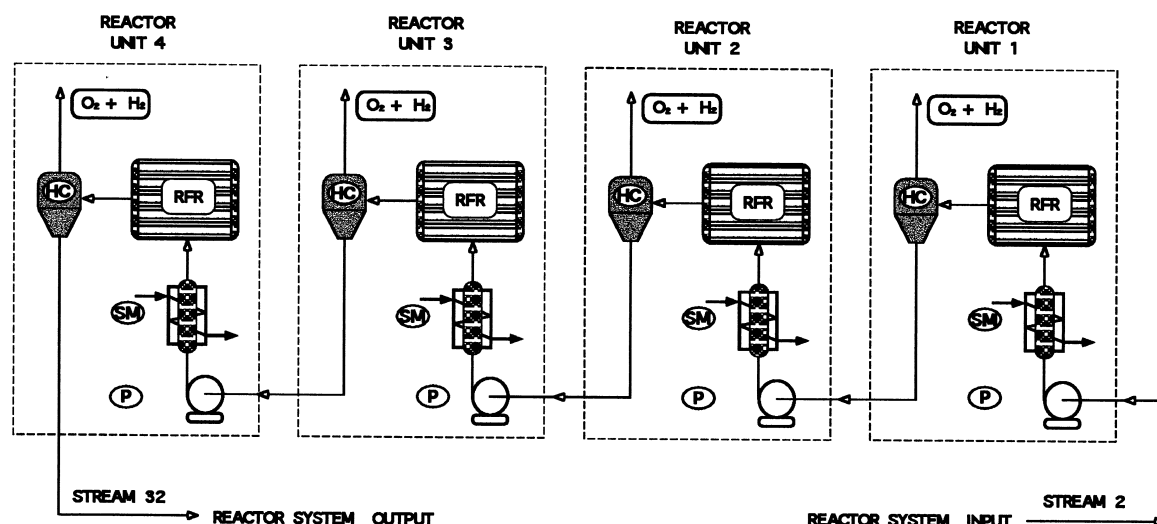


Fig. 3. Example of an electrochemical reactor system (ERS) for soybean oil electrohydrogenation containing four multielement radial flow reactors (RFR), pumps (P), static mixers (SM), and hydrocyclones (HC).

the hydrogenation current efficiency) and that there is no build-up of potentially explosive  $H_2$  gas. The reactor units in the ERS are electrically interconnected in parallel using common cathode and anode buses in order to maintain the same electric current to each unit. A modular reactor layout was chosen so that: (i) the stability of the two-phase electrolyte can be maintained by intermediate remixing between reactor units, (ii) plant capacity can be altered simply by adding or removing reactor units, without changing the reactor's primary operating conditions (current density and electrolyte oil content), (iii) the temperature condition in the reactors can be controlled by the jacketed water-cooled static mixers, and (iv) the continuous operation of the process can be insured by including a stand-by reactor unit that is properly manifolded to the reactor system, should one reactor be shut down for maintenance.

In the present analysis, we have assumed that the industrial-size reactors would contain anode/cathode elements with the same radial dimensions (thicknesses of the porous ceramic tubes and Raney nickel bed) and a similar electrolyte flow pattern as the inward radial-flow laboratory-scale prototype reactor discussed in [5]. The radial-flow design was chosen so that each anode/cathode tubular element would scale linearly with tube length, where the key scale-up parameter is the geometric cathode surface area at the inner radius of the Raney nickel bed (i.e., the geometric cathode area at that portion of the bed closest to the anode). This same cathode area is used to define the applied current density during reactor operation. In order to achieve high production rates of hydro-oil, this area is increased by employing multiple long tubes in a common shell. In the present study, we have arbitrarily set the anode/cathode tube length at 200 cm and the number of tubes per reactor at 200. The design specifications for such a multiple anode/cathode element reactor are listed in Table 2.

After exiting the ERS, the oil is separated from the solvent/supporting electrolyte, cleaned, and dried.

There is no need to isolate hydrogenated oil product from unreacted starting material and in this regard the product purification steps for the oil hydrogenation process are simple and straightforward. The separation loop is comprised of the following operations: (i) two-phase gravity separators SEP1 and SEP2, where oil and aqueous phases are separated, (ii) evaporator EV to remove *t*-butanol solvent from the hydrogenated soybean oil, (iii) dryer DR to remove traces of water and *t*-butanol from the final hydrogenated soybean oil product, (iv) condenser CR to recover water and *t*-butanol vapours from EV and DR, (v) reverse-osmosis membrane separations module, RO, to regenerate a concentrated TEATS solution from a diluted salt water stream, and (vi) three mixing tanks, MIX2, MIX3 and MIX4. The separation loop has only one input (stream 5) and two output streams, stream 17 containing purified partially hydrogenated soybean oil product and stream 6 with the recovered solvent/supporting electrolyte. The separation loop operates as follows.

Table 2. Geometric dimensions and electrolyte flowrate for proposed commercial-size radial-flow Raney nickel powder reactor

Dimension	Value
Length of ceramic tubes	200 cm
Number of tubes per reactor	200
Reactor shell diameter	100 cm
ID of inner ceramic tube*	2.22 cm
OD of inner ceramic tube*	3.15 cm
ID of outer ceramic tube*	4.60 cm
OD of outer ceramic tube*	5.60 cm
Thickness of Raney nickel bed*	0.725 cm
Apparent cathode area per tube at the inner diameter of the nickel bed	1979 cm <sup>2</sup>
Total apparent cathode area per reactor	395 841 cm <sup>2</sup>
Specific electrolyte velocity*	3.0 ml min <sup>-1</sup> cm <sup>-2</sup>
Volumetric flow rate (mass flow rate)	1188 dm <sup>3</sup> min <sup>-1</sup> (64 838 kg h <sup>-1</sup> )

\* Based on the laboratory-scale radial-flow reactor in [5].

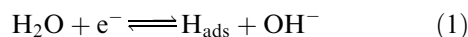
Stream 5, which comes from the reaction loop, first enters phase separator SEP1 where the reaction medium's two phases are separated. The bottom (aqueous) fraction (stream 8) carries almost all of the water and TEATS salt and some *t*-butanol (there is no oil in stream 8). The top oil fraction (stream 7) contains all of the oil, some *t*-butanol, and traces of water and TEATS. Stream 7 is fed to evaporator EV to remove the *t*-butanol from the hydrogenated soybean oil (stream 10 contains only *t*-butanol). The evaporator's liquid output, stream 9, contains hydrogenated soybean oil with small amounts of water and TEATS. This stream is mixed with pure water (stream 11) in mixer MIX3 to extract traces of TEATS from the hydrogenated soybean oil. The two-phase solution exiting MIX3 (stream 12) enters a second phase separator (SEP2) where the oil-rich top layer is removed via stream 13 and then is pumped through dryer DR to remove trace amounts of water and alcohol from the hydrogenated soybean oil product. The water vapour coming out of dryer DR (stream 16) is mixed in unit MIX4 with the condensed *t*-butanol vapour that emerges from evaporator EV. This mixture (stream 18) is condensed in CR and sent to another mixing tank, MIX2. The bottom aqueous phase from separator SEP2 (stream 14) contains traces of TEATS diluted in a large volume of water. TEATS is concentrated in a reverse osmosis membrane device (RO) that has two outputs, the brine or concentrated TEATS solution (stream 15) that is pumped to tank MIX2 and the purified water stream that is recycled to MIX3 (stream 11). Solvent/salt recycle streams 8, 15 and 19 are mixed in tank MIX2 and then sent back to the reactor loop via stream 6.

### 3. Reactor model and process simulation code

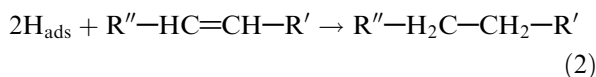
#### 3.1. Porous electrode reactor model

A semiempirical model for the radial-flow Raney nickel powder reactor was formulated to predict soybean oil hydrogenation current efficiencies as a function of the electrolyte oil content and applied current density using porous electrode theory and a phenomenological reaction rate expression for hydrogen evolution. The resulting Fortran computer code was then linked to the PRO/II software in order to simulate the oil hydrogenation plant shown in Fig. 2.

In the reactor model, the two-phase oil/water/*t*-butanol/TEATS electrolyte was treated as a pseudo-single phase solution and only reactions occurring at the cathode were considered. The anode reaction (the oxidation of water to O<sub>2</sub>) was assumed to have no effect on the soybean oil hydrogenation rate and current efficiency. In the model, all reactions were assumed to be kinetically controlled, with a Volmer-Tafel mechanism [8] for hydrogen evolution on Raney nickel powder. The electrochemical reaction on the nickel catalyst surface was the production of adsorbed atomic hydrogen from water via the Volmer reaction step,



H<sub>ads</sub> then either reacted with the unsaturated constituents of soybean oil to form a partially hydrogenated oil product (the chemical catalytic step) or combined with another adsorbed hydrogen atom to form molecular hydrogen gas (the Tafel or recombination step),



The system coordinates for the radial-flow reactor model were defined as follows:  $r = 0$  was the central axis of the reactor (the centreline of the anode rod),  $r = R_1$  was located at the front (inner) radius of the porous nickel bed and  $r = R_2$  was at the back or outer radius of the catalyst bed. In the model, all changes in reaction rates were assumed to take place in the radial direction. Since the hydrogen consumption reactions given by Equations 2 and 3 occur simultaneously and compete for H<sub>ads</sub> on the catalyst surface, the following mass balance equation for H<sub>ads</sub> can be written,

$$2 n_{\text{db}} \hat{j}_2 = \hat{j}_1 - 2 \hat{j}_3 \quad (4)$$

where  $n_{\text{db}}$  is the number of double bonds reduced in one mole of soybean oil, and  $\hat{j}_1$ ,  $\hat{j}_2$  and  $\hat{j}_3$  are the average rates of H<sub>ads</sub> generation (Equation 1), oil hydrogenation (Equation 2) and H<sub>2</sub> evolution (Equation 3) in the packed bed (with units of gmoles per unit time per unit surface area of catalyst). These rates were computed as integral (spatial) averages of the local reaction rates along the radial thickness of the porous Raney nickel cathode,

$$\hat{j}_i = \frac{\int_{R_1}^{R_2} j_i(r) r \, dr}{\int_{R_1}^{R_2} r \, dr} \quad i = 1, 2, 3 \quad (5)$$

The average soybean oil hydrogenation current efficiency for the entire nickel bed cathode (denoted CE), is defined as the average rate of hydrogen addition to the oil divided by the average rate of H<sub>ads</sub> generation,

$$\text{CE}(\%) = \frac{2 n_{\text{db}} \hat{j}_2}{\hat{j}_1} \times 100 \quad (6)$$

This equation was rewritten in terms of  $\hat{j}_3$  and  $\hat{j}_1$  by combining Equations 4-6,

$$\text{CE}(\%) = \left[ 1 - \frac{2 \int_{R_1}^{R_2} j_3(r) r \, dr}{\int_{R_1}^{R_2} j_1(r) r \, dr} \right] \times 100 \quad (7)$$

The local reaction rate for the Volmer step,  $j_1(r)$  in Equation 7, was described by a Butler-Volmer kinetic expression [8, 9],

$$j_1(r) = i_{0,1} \frac{1}{F} \left[ \exp\left(-\frac{\alpha F}{RT} \eta(r)\right) - \exp\left(\frac{(1-\alpha)F}{RT} \eta(r)\right) \right] \quad (8)$$

where  $i_{o,1}$  is the exchange current density ( $\text{A cm}^{-2}$  of catalyst surface). (All other symbols are explained in the initial listing.) As shown previously [5, 6], soybean oil hydrogenation current efficiencies decreased ( $\text{H}_2$  evolution rates increased) with increasing electrolyte oil content and increasing current density. To account for this behaviour, the following empirical expressions for  $i_{o,1}$  and  $j_3(r)$  were added to the model:

$$i_{o,1} = K_1 \ln \left[ \frac{C_{\text{oil}}}{C^*} \right] \quad (9)$$

$$j_3(r) = K_2 \ln \left[ \frac{C_{\text{oil}}}{C^*} \right] \left[ \frac{j_1(r)}{j^*} \right]^{K_3} \quad (10)$$

where  $K_1$  ( $\text{A cm}^{-2}$  of catalyst area),  $K_2$  ( $\text{gmol s}^{-1} \text{cm}^{-2}$  of catalyst area) and  $K_3$  (dimensionless) are constants,  $C_{\text{oil}}$  is the oil content in the reaction medium (with units of wt:vol%),  $C^*$  is a reference oil concentration (set at 1.0 wt:vol%) and  $j^*$  is a reference reaction rate of the Volmer reaction (set at  $1.0 \text{ gmol cm}^{-2} \text{ s}^{-1}$ ). The form of Equation 10 assumes that the concentration of  $\text{H}_2$  gas dissolved in the reaction medium is low at the reaction conditions for soybean oil hydrogenation (i.e., the backward reaction of Equation 3 can be neglected). Both Equations 9 and 10 were arrived at by means of a trial and error search of different empirical  $i_{o,1}$  and  $j_3$  functions. The relationships given above allowed the model to match experimental current efficiency data with the laboratory-scale reactor shown in Fig. 1 of [5], as will be discussed below.

To calculate the soybean oil current efficiency as defined by Equation 7 for a given electrolyte oil content,  $j_1(r)$  was computed in the catalyst packed bed using porous electrode theory [10]. The relevant equations were the Butler–Volmer kinetic expression (Equation 8) and the following charge balance and solution-phase Ohm's law equations,

$$\nabla \cdot [i(r)] = \frac{di(r)}{dr} + \frac{i(r)}{r} = -aF j_1(r) \quad (11)$$

$$\kappa \nabla \eta(r) = \kappa \frac{d\eta(r)}{dr} = i(r) \quad (12)$$

where  $i(r)$  is the current density in solution ( $\text{A cm}^{-2}$ ) and  $\kappa$  is the electrolyte conductivity ( $\Omega^{-1} \text{cm}^{-1}$ ). The parameter  $a$  in Equation 11 is defined as the specific area per unit volume of Raney nickel powder catalyst ( $\text{cm}^{-1}$ ) and is used to relate the rate of atomic hydrogen production per unit surface area of catalyst ( $j_1$ ) with the current density,  $i(r)$ , which is based on the geometric cross sectional area of the nickel bed. After combining Equations 8, 11 and 12, the porous electrode model was condensed into a single differential equation,

$$\frac{d^2 \eta(r)}{dr^2} + \frac{1}{r} \frac{d\eta(r)}{dr} + \frac{a}{\kappa} i_{o,1} \left[ \exp \left( -\frac{\alpha F}{RT} \eta(r) \right) - \exp \left( \frac{(1-\alpha)F}{RT} \eta(r) \right) \right] = 0 \quad (13)$$

Boundary conditions for Equation 13 at the front and back of the Raney nickel bed for constant current

density ( $i = i_{\text{app}}$ ) reactor operation are as follows:

(i) at  $r = R_1$

$$\kappa \frac{d\eta}{dr} = i_{\text{app}} \quad (14)$$

(ii) at  $r = R_2$

$$\kappa \frac{d\eta}{dr} = 0 \quad (15)$$

Equation 13 was solved on a computer using standard quasi-linearization/finite-difference numerical techniques. Once  $\eta(r)$  was computed for a given set of operating conditions, the reaction rates  $j_1(r)$  and  $j_3(r)$  were determined from Equations 8 and 10, and the soybean oil current efficiency was calculated from Equation 7. Parameters for the laboratory-scale Raney nickel powder radial-flow reactor and an electrical conductivity relationship for the oil/electrolyte reaction medium are listed in Table 3. The conductivity of the oil/electrolyte emulsion was measured experimentally as a function of oil content and water/*t*-butanol solvent composition at  $25^\circ\text{C}$ ; this conductivity function was then corrected for temperature and the Raney nickel bed porosity [11]. The model also contained three constants ( $K_1, K_2$  and  $K_3$ ) which were not known *a priori* for the soybean oil hydrogenation reaction scheme. These parameters were found by matching soybean oil hydrogenation current efficiencies from 15 different radial-flow reactor experiments [5] with the corresponding predictions of the model. The resulting values of these parameters, which allowed the model to predict experimental current efficiencies with an average error of 4%, were:  $K_1 = 4.8 \times 10^{-9} \text{ A cm}^{-2}$ ,  $K_2 = 2.8 \times 10^{13} \text{ gmol cm}^{-2} \text{ s}^{-1}$  and  $K_3 = 2.3$ . A comparison of experimental and predicted oil hydrogenation current efficiencies is shown in Fig. 4. Although the empirical model works well and is useful in performing computer-aided preliminary plant design and cost calculations, it is only intended to reproduce experimental oil hydrogenation current efficiency data between 10 and  $45 \text{ mA cm}^{-2}$ .

In addition to predicting the soybean oil hydrogenation current efficiency, the model also generated Raney nickel bed radial-direction profiles for the

Table 3. Kinetic and geometric parameters and physical property data for the Raney nickel porous electrode model

Parameter	Value
Charge-transfer coefficient ( $\alpha$ )	0.5
Inner radius of bed ( $R_1$ )	1.575 cm
Outer radius of bed ( $R_2$ )	2.30 cm
Raney nickel powder specific surface area ( $a$ )	$1.47 \times 10^6 \text{ cm}^{-1}$
Electric conductivity ( $\kappa$ ) of the oil/electrolyte dispersion at $25^\circ\text{C}$	$0.0121 \times \exp[-0.11 C_{\text{oil}} - 0.02 C_{\text{B}}]^*$

\* Electrical conductivity was determined experimentally [11], with  $C_{\text{oil}}$  (soybean oil concentration) units of wt:vol% and  $C_{\text{B}}$  (*t*-butanol concentration) units of vol%.

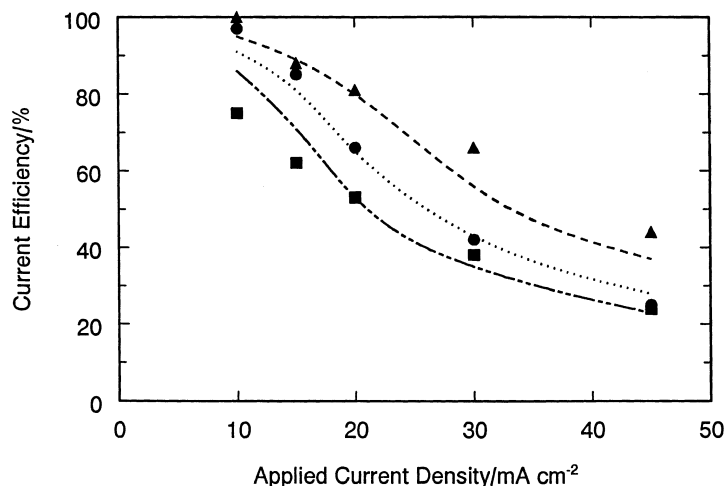


Fig. 4. Comparison of experimental data and model predictions for the current efficiency of soybean oil hydrogenation in the laboratory-scale radial flow reactor. Reaction conditions: 75°C temperature, 6.55 cm tubular reactor length, 300 ml min<sup>-1</sup> electrolyte flow rate, 50:50 vol % water:*t*-butanol solvent, 0.5 M TEATS supporting electrolyte. Experimental data: (▲) 10, (●) 25 and (■) 45 wt:vol % oil. Model predictions: (-----) 10, (.....) 25 and (—) 45 wt:vol % oil.

overpotential ( $\eta$ ) and the individual reaction rates for H<sub>ads</sub> formation ( $j_1$ ) and H<sub>2</sub> evolution ( $j_3$ ). These profiles were typical of porous electrode theory [10, 12] and showed that: (i) The overpotential was highest at the front face of the cathode bed (that portion closest to the anode) and decreased exponentially with distance away from the cathode/anode interface due to ohmic resistance to current flow in the solution phase of the porous nickel electrode, (ii) the overpotential profile was more negative (cathodic) when the applied current density was increased, and (iii) the overpotential dropped to zero before the back of the bed was reached for all current densities examined (this result could be used to determine the optimum Raney nickel bed thickness, although this was not performed in the present study due to the empiricism of Equations 9 and 10).

### 3.2. Process simulation code

The electrocatalytic soybean oil hydrogenation plant shown in Fig. 2 was simulated using the PC-based software package PRO/II (version 3.3.2). The electrochemical porous electrode reactor model, presented in the preceding section, was linked to the simulation code as a 'user defined' Fortran subroutine. Process simulation calculations were performed for different reactor operating conditions, that is, for different concentrations of soybean oil in the reactor feed stream and different applied current densities. The computed results from the software package included: (i) mass and energy balances for each unit operation (including the electrochemical reactor system), (ii) process stream compositions, and (iii) the electrochemical reactor size and performance results (current efficiency and power requirement). The first 50 lines of input code for the process simulation are listed in Fig. 5.

In PRO/II process simulations, input data are divided into five main categories: general data, component data, thermodynamic data, stream data, and

```

GENERAL DATA
  TITLE PROJECT= OIL HYDROGENATION PLANT
  DIMENSION SI, TEMPERATURE=C, PRES=ATM
  TOLERANCE STREAM=0.005,-1.0,0.01,0.01, TEMP=-1.0
  CALCULATION TRIALS=10
  SEQUENCE UDS01,CAL01,HC,SPT,SEP1,EV,MIX3,SEP2,RO,DR,MIX4,&
    CR,MIX2,MIX1
  PRINT INPUT=NONE,&
  STREAM=COMPONENT,&
  RATE=WT, PERCENT=WT, MBALANCE
$
COMPONENT DATA
  LIBID 1,OLEIC/2,LINOLEIC/3,H2O/4,TBA/5,BRK/6,H2/7,O2
$
THERMODYNAMIC DATA
  METHOD SYSTEM = NRTL, HENRY
  HENRY
  SOLUTE 6, 7
$
STREAM DATA
  PROPERTY STREAM=1, TEMP=70, PHASE=L, PRES=1,&
  RATE(KG/HR)=360, COMP(WT)=1.45/2.55
  PROPERTY STREAM=WM, TEMP=70, PHASE=L, PRES=1,&
  RATE(KG/HR)=8.74115, COMP(WT)=3,100
  PROPERTY STREAM=2, TEMP=70, PHASE=L, PRES=1,&
  RATE(KG/HR)=64838.58,&
  COMP(WT)=1,7.32/2,2.58/3,42.00/4,33.17/5,14.92
  PROPERTY STREAM=4, TEMP=70, PRES=1, RATE(KG/HR)=63000
  PROPERTY STREAM=6, TEMP=70, PRES=1, RATE(KG/HR)=1300
  PROPERTY STREAM=11, TEMP=70, PRES=1.0, RATE(KG/HR)=1080, &
  COMP(WT)=3,100
  PROPERTY STREAM=17, TEMP=70, PRES=1.0, RATE(KG/HR)=360.79, &
  COMP(WT)=1,75.69/2,24.31
$
UNIT OPERATION DATA
$
MIXER          UID=MIX1
  FEED 1,WM,4,6
  PROD L=2
$
US2           UID = UDS01
  FEED 2
  PROD 3
  RPARAM 0.03
$
CALC          UID = CAL01
  DIMENSION P(1)
  SEQUENCE STREAM = WM
  DEFINE P(1) AS US2 = UDS01, PARA(2)
  PROCED
  CALL SRVSTR(SCWR, P(1), WM, 3, 3)
  RETURN
$
SEPARATOR     UID=HC
  FEED 3
  OVHD STRM=31, PHASE=V, TEMP=70
  BTMS STRM=32, PHASE=L, TEMP=70
  FOVHD 1,0,0/2,0,0/3,0,0/4,0,0/5,0,0/6,1,0/7,1,0

```

Fig. 5. First 50 lines of PRO/II code for the simulation of the soybean oil hydrogenation plant shown in Fig. 2.



unit operations data. The reader should refer to the PRO/II input manual for complete information about specific simulator features and coding options [13]. The 'general data' section lists global defaults for the entire simulation. In Fig. 5, the general data code specifies the units convention for input and output data (SI units, with overrides for temperature and pressure), stream tolerances for iterative solutions during unit operations calculations, the maximum number of recycle calculation trials and the sequence in which the unit operations calculations are to be performed. The PRINT INPUT and STREAM statements were used to control the printing of input and output data (in the present program all stream component flow rates and the overall mass balance for each stream using a weight basis were printed).

The 'component data' statement defines the pure and pseudo-components in the process problem and assigns an identification number to each component. PRO/II contains an extensive data base of over 1550 pure components. Water and *t*-butanol were selected from this list. Soybean oil and tetraethylammonium *p*-toluenesulfonate (TEATS) were not available as library components and had to be replaced by data base compounds having similar physical and chemical properties. TEATS, which does not undergo any chemical change during the soybean oil hydrogenation process, was replaced by potassium bromide (since the anode reaction was not modelled, there was no bromine generation in the reactor). It was assumed that soybean oil was composed of library components oleic acid and linoleic acid (the two primary fatty acid constituents of soybean oil). The chemical properties of soybean oil, oleic acid (an 18 carbon fatty acid with a single double bond) and linoleic acid (an 18 carbon fatty acid with two double bonds) are almost identical and a mixture of 45 wt % oleic acid and 55 wt % linoleic acid produced a starting material with the same degree of unsaturation as that of unreacted soybean oil [11].

The 'thermodynamic data' category specifies the method of calculating thermodynamic quantities such as liquid-phase activities, ideal vapour enthalpies, and mixture densities. In the present problem, the nonrandom two liquid (NRTL) model was selected for all thermodynamic property calculations (Fig. 5). The HENRY option in the code applies to prestored Henry's law electrolyte solubility data for O<sub>2</sub> and H<sub>2</sub> gases (components 6 and 7, respectively).

The 'stream data' section assigns a stream identifier to each external stream that feeds into the flow-sheet, along with the component flow rates, temperatures and pressures of the external streams. Additionally, estimates of the composition, flow rate and thermal properties of recycle streams (which are needed to initiate iterative calculations) are specified in this section of the code. Table 4 lists the known and estimated conditions of the process streams for the  $3.0 \times 10^6 \text{ kg y}^{-1}$  soybean oil hydrogenation plant. The oil/electrolyte composition at which the electrochemical reactor operates is specified in the simula-

Table 4. Stream input data for simulation of a  $3.0 \times 10^6 \text{ kg y}^{-1}$  electrocatalytic oil hydrogenation plant

Stream	Flow rate /kg h <sup>-1</sup>	Operating conditions
1	360*	Soybean oil, 70 °C, atmospheric pressure
WM	†	Water, 70 °C, atmospheric pressure
2	64 838*	Reactor input, 70 °C, atmospheric pressure
3	†	Reactor output, 70 °C, atmospheric pressure
4	63 000‡	Recycle stream, 70 °C, atmospheric pressure
6	1 300‡	Recycle stream, 70 °C, atmospheric pressure
11	1 080*	Water, 70 °C, atmospheric pressure

\* process specification.

† determined by the reactor model.

‡ initial estimates.

tion input code by the (fixed) component composition of stream 2. Process design calculations were based on an electrolyte composition which was identical to that used in the laboratory-scale reactor experiments and the porous electrocatalytic reactor modelling studies, that is, 0.5 M TEATS, 50:50 vol % *t*-butanol:water, and either a 10 wt:vol %, 25 wt:vol %, or 45 wt:vol % oil:electrolyte composition (as noted above, the oil was replaced by an oleic acid/linoleic acid mixture and all concentrations were converted to units of kg h<sup>-1</sup> for data input into the PRO/II program). The flow rates entered for recycle streams 4 and 6 were only initial estimates; PRO/II calculated the actual composition and flow rates of these streams by means of an iterative numerical scheme. The mass flow rate of stream 11 was fixed at 1080 kg h<sup>-1</sup> so that the ratio of water to oil in mixing tank MIX3 (the TEATS extractor) was equal to 3 (Table 1).

The 'unit operations data' section contains lines of code that are used to define the process equipment in the oil hydrogenation plant. PRO/II recognizes two types of unit operations: (i) library unit operations that are fully described in the simulation software code and (ii) user defined subroutines that model unit operations not available in the simulator, such as the packed bed electrochemical reactor system for the oil hydrogenation process. In Fig. 5, unit operations statements are listed for mixer MIX1, phase separator HC, and the radial-flow electrochemical reactor network. Feed and exit streams for each unit are identified, along with relevant stream constraints and process specifications (see [13] for additional details). The CALC (calculator) module in Fig. 5 does not denote a unit operation but refers to a Fortran 77 utility module built into PRO/II that retrieved the water consumption rate from the porous electrode model, for a given applied constant current density and solution flow rate/feed composition, and assigned it to the flow rate of the water make-up stream (stream WM).

In the flow sheet simulation code, the radial flow reactor model for the determination of the oil hydrogenation current efficiency was expanded to include the following additional calculations: (i) the reactor's power requirements, (ii) the optimum cata-

Table 5. Performance data of the radial flow reactor in simulation of the electrochemical process

Operating conditions	$i/\text{mA cm}^{-2}$	CE /%	Reactor units*	Power /kW	Heat duty / $10^6 \text{ kJ h}^{-1}$	SEC <sup>†</sup> /kJ g <sup>-1</sup>	Total current /A
Oil content: 10 wt.vol%	10	95	5.6	140	0.417	1.40	22 100
	15	89	4.0	208	0.653	2.08	23 600
	20	80	3.3	298	0.960	2.98	26 300
	30	56	3.2	618	2.05	6.18	37 900
	45	37	3.2	1370	4.62	13.6	57 400
Oil content: 25 wt.vol%	10	91	5.8	166	0.507	1.66	23 100
	15	81	4.4	264	0.842	2.64	26 000
	20	65	4.1	424	1.38	4.24	32 400
	30	43	4.1	927	3.10	9.27	48 900
	45	29	4.1	2050	7.01	20.5	74 000
Oil content: 45 wt.vol%	10	87	6.1	209	0.658	2.09	24 300
	15	71	5.0	366	1.19	3.66	29 800
	20	53	5.0	634	2.10	6.34	39 800
	30	35	5.1	1400	4.74	14.0	60 200
	45	23	5.1	3120	10.7	31.2	91 200

\* Each reactor unit contains 200 tubular anode/cathode elements, each tube is 200 cm in length. For design and cost calculations, fractional reactor units were increased to the next whole number.

† Specific energy consumption.

lyst thickness (defined as that portion of the Raney nickel bed where 95% of the oil was being hydrogenated), (iii) the required number of 200 cm long, 200 anode/cathode tube reactor units, and (iv) the reactor's heat duty. No attempt was made to optimize the Raney nickel bed thickness in the present study, due to the empiricism of the reaction rate equations in the porous electrode reactor model. The power requirement for the electrochemical reactor system was computed as the product of the total current,  $I$  (A), and the absolute value of the voltage drop between the anode and cathode (V). The radial flow reactor model calculated the total current for the reactor system from the process specification of a 20% reduction in the number of double bonds, the feed flow rate and the current efficiency of the hydrogenation reaction (computed from Equation 7) according to

$$I = \frac{\text{FEED} \times \text{CB} \times \text{CONV}}{\text{CE}} \quad (16)$$

where FEED is the mass flow rate in stream 1 ( $100 \text{ g s}^{-1}$ ), CB is the charge (C) required to fully hydrogenate 1 g of soybean oil ( $1054 \text{ C g}^{-1}$ ), CONV is the prespecified percentage conversion in the number of double bonds in the oil feed (20%), and CE is the computed current efficiency (%). The voltage drop in the reactor was computed as the sum of the anode potential (1.23 V for oxygen evolution, assuming no anodic overpotentials), the absolute value of the voltage at the front face of the cathode bed (as determined by the reactor model) and the ohmic resistance drop in the oil/electrolyte solution between the anode and cathode. Heat generated in the electrocatalytic reactors had two sources: the exothermic heat of reaction during the hydrogenation of the oil's double bonds, where a  $1^\circ\text{C}$  temperature rise has been reported for each unit decrease in the oil's iodine value (which is a quantitative measure of

the oil's degree of unsaturation) [14], and electrolyte heating due to the passage of current through an electrolyte of finite electrical conductivity.

Based on the computed current efficiency and total applied current, the radial flow reactor model in the PRO/II simulation calculated the consumption rates ( $\text{kg h}^{-1}$ ) for linoleic acid and water and the formation rates ( $\text{kg h}^{-1}$ ) of oleic acid, hydrogen, and oxygen. These results were then combined with the mass flow rates of feed stream 2 to compute the individual component mass flows leaving the reactor system in stream 3. The composition of stream 3 was transferred back to the main PRO/II simulation program in order to continue with unit operations calculations downstream from the reactor network.

The key feature of the PRO/II input code was the electrocatalytic reactor unit operation module, which was incorporated into the simulation code as a user defined subroutine (UDS). In the simulation of the oil hydrogenation plant (cf. Fig. 5), the UDS for the electrochemical reactor was labelled US2, with feed and outlet streams 2 and 3, respectively. The two operating variables for the reactor model were: (i) the applied current density which was entered in the simulation input file as an operating parameter (RPARM) and (ii) the electrolyte composition (oil content) for stream 2, which was defined in the 'stream data' category, as discussed above. The unit operation block US2 consists of the Fortran program for the electrochemical reactor model presented above plus subroutines that: (i) print the radial-flow reactor model results and (ii) link the reactor model with the PRO/II simulation program by retrieving the applied current density and the feed stream component flow rates for the electrochemical reactor system from the main input code, constructing the flow rate and composition of the product stream emerging from the ERS, and transferring results from the re-

actor model to the main simulation code (e.g., the oil hydrogenation current efficiency, the number of reactor units, the total anode/cathode voltage drop, the total heat duty, the specific energy consumption, and the optimum nickel bed thickness). For additional details regarding user defined subroutines in PRO/II simulations, the reader should consult [11, 13 and 15].

#### 4. Results and discussion

The heat and mass balance simulation program for the electrocatalytic hydrogenation plant was used to calculate the plant size and evaluate production costs for five different current densities (10, 15, 20, 30 and 45 mA cm<sup>-2</sup>) and three different electrolyte oil contents (10, 25 and 45 wt:vol %). Table 5 lists performance data (the required number of 200 tube reactor units and the electrical energy demand) for the radial-flow reactor, as computed in the PRO/II simulation code. When the applied current density was increased at a given oil content or when the oil content of the reaction medium was increased at a fixed current density, the current efficiency for soybean oil hydrogenation decreased, resulting in a larger demand for electrical power, an increase in the reactors' heat duty, and a higher specific energy consumption. This behaviour is summarized graphically in Fig. 6 for different operating conditions. When the current density is less than 20 mA cm<sup>-2</sup>, the total number of reactor units required to process 3.0 × 10<sup>6</sup> kg y<sup>-1</sup> of soybean oil decreases significantly with increasing current density. Above 20 mA cm<sup>-2</sup>, the number of required reactors remains constant and independent of the applied current density. This result can be explained by noting that the required number of reactor units for the process is dependent on the net oil hydrogenation rate, which is equal to the product of the applied current density and hydrogenation current

efficiency. Although the current efficiency for oil hydrogenation decreased with increasing current density, the product of current efficiency and current density remains essentially constant for current densities ≥ 20 mA cm<sup>-2</sup>. This situation can be regarded as a kinetically controlled limiting current density, where the oil hydrogenation reaction rate is no longer dependent on the electrochemical rate of H<sub>ads</sub> generation on the catalyst surface. The high current efficiencies at low current densities (i.e., 10 mA cm<sup>-2</sup>) results in low electric costs (low specific power requirements), but the capital cost of the reactor system is high because more reactor units are required to obtain the same net oil hydrogenation rate.

The capital costs of the various unit operations in the electrocatalytic soybean oil hydrogenation plant are presented in Table 6 for five different applied current densities and three different oil concentrations in the electrolyte. The analysis took into account only the capital investment for equipment; the costs of land, process utilities, service facilities, buildings, and other installations were not considered. Equipment costs were based on the specifications of the unit operations (such as those listed in Table 1) and price quotes from commercial distributors (see [11] for details of the cost calculations). The cost of the electrochemical reactors was based on individual vendor price quotes of the reactor shell, ceramic tubes, catalyst, DSA rods, electric rectifier, static mixer, pump and hydrocyclone. Piping and instrumentation costs were estimated as a percentage of the purchased equipment cost (36% and 13%, respectively) [16]. All process equipment and piping were constructed of stainless steel. The results in Table 6 show comparatively low capital costs (\$710 000–\$830 000) when the electrolyte contained either 10 wt:vol % oil (at applied current densities between 15 and 45 mA cm<sup>-2</sup>) or 25 wt:vol % oil (at applied current densities of 15–30 mA cm<sup>-2</sup>). For a given oil content, there was a mid-range current density (15–20 mA cm<sup>-2</sup>) that minimized the capital cost of the plant. At lower current densities, the capital cost was high because the process required more reactor units to hydrogenate the oil. When the current density and oil concentration were high, the capital cost was high due to an increase in rectifier costs (e.g., the low conductivity of a high oil content electrolyte produced a substantial increase in the anode–cathode voltage drop). A global minimum in capital cost (\$710 000) was identified for an oil content of 10 wt:vol % and an applied current density of 20 mA cm<sup>-2</sup>. It is interesting to note that the capital cost for the hydro-oil purification and solvent/supporting electrolyte recycle equipment did not change significantly with the composition of the reaction medium; \$190 000 at 10 wt:vol % oil, \$170 000 at 25 wt:vol %, and \$150 000 at 45 wt:vol %. The small decrease in capital cost for the higher oil content feeds was due to a decrease in the volume of *t*-butanol within the separation loop.

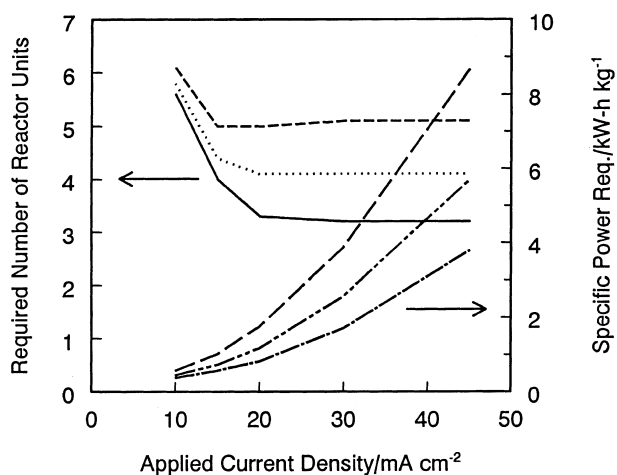


Fig. 6. Effect of applied current density and electrolyte oil content on the number of reactor units and the reactor's specific power requirements for a 3.0 × 10<sup>6</sup> kg y<sup>-1</sup> soybean oil electrocatalytic hydrogenation plant. Number of reactor units for (—) 10, (·····) 25 (-----) 45 wt:vol % oil. Specific power requirements for (—) 10, (—) 25 and (—) 45 wt:vol % oil.

Table 6. Capital costs for the electrocatalytic hydrogenation process

Plant capacity:  $3.0 \times 10^6 \text{ kg y}^{-1}$ 

Operating conditions	$i/\text{mA cm}^{-2}$	Capital costs for individual unit operations equipment, instrumentation and piping / $10^3$ US\$										Total capital cost / $10^3$ US\$
		ERS	SEP1&2	SPT	EV	MIXERS	RO	CR	DR	Total UO	Instrum. and piping	
Oil content	10	700	43	3.5	35	34	40	18	15	188.5	92	980
10 wt:vol %	15	510	43	3.5	35	34	40	18	15	188.5	92	790
	20	430	43	3.5	35	34	40	18	15	188.5	92	710
	30	480	43	3.5	35	34	40	18	15	188.5	92	760
	45	480	43	3.5	35	34	40	18	15	188.5	92	760
Oil content	10	727	37	3.5	23	34	40	14	15	166.5	81	980
25 wt:vol %	15	561	37	3.5	23	34	40	14	15	166.5	81	810
	20	586	37	3.5	23	34	40	14	15	166.5	81	830
	30	586	37	3.5	23	34	40	14	15	166.5	81	830
	45	886	37	3.5	23	34	40	14	15	166.5	81	1100
Oil content	10	762	35	3.5	16	34	40	11	15	154.5	75	990
45 wt:vol %	15	632	35	3.5	16	34	40	11	15	154.5	75	860
	20	692	35	3.5	16	34	40	11	15	154.5	75	920
	30	704	35	3.5	16	34	40	11	15	154.5	75	930
	45	1400	35	3.5	16	34	40	11	15	154.5	75	1600

There were three major operating (utility) costs for the electrocatalytic oil hydrogenation process: electrical energy (for the electrochemical reactors and pumps), cooling water (for the evaporators and water-cooled static mixers in the ERS) and low-pressure steam (for the evaporators). The results of the operating costs calculations (Table 7) were based on the utility requirements of each unit operation (as computed from the PRO/II simulation) and the annual production rate of hydro-oil. All calculations used an

electricity cost of \$0.059 per kWh (Detroit Edison, April 1991), a cooling water cost of \$4.22 per  $100 \text{ m}^3$  (Tektronix, Oregon, June 1994) and a low-pressure steam cost of \$2.30 per 1000 kg [16]. The operating cost per kilogram of oil product was found to be dominated by the electrical energy cost which, in turn, was controlled by the performance of the electrochemical reactors, that is, operating costs were low for those reactor operating conditions which resulted in high oil hydrogenation current efficiencies. When

Table 7. Process utility requirements and costs for the electrocatalytic soybean oil hydrogenation plant

Operating conditions	$i/\text{mA cm}^{-2}$	Process utilities requirements*						Operating cost <sup>†</sup>
		Electrical energy		Cooling water		Steam		
		/kW	Cost <sup>‡‡</sup>	/ $\text{m}^3 \text{ h}^{-1}$	Cost <sup>§§</sup>	/kg $\text{h}^{-1}$	Cost <sup>##</sup>	
Oil content:	10	237	0.039	18.8	0.0022	207	0.0013	0.043
10 wt:vol %	15	281	0.046	24.4	0.0029	207	0.0013	0.049
	20	361	0.059	31.7	0.0037	207	0.0013	0.064
	30	680	0.11	57.8	0.0068	207	0.0013	0.13
	45	1430	0.23	119	0.014	207	0.0013	0.25
Oil content:	10	266	0.043	15.8	0.0018	108	0.00066	0.046
25 wt:vol %	15	343	0.053	23.8	0.0029	108	0.00066	0.057
	20	499	0.081	36.7	0.0044	108	0.00066	0.086
	30	1000	0.16	77.9	0.0092	108	0.00066	0.17
	45	2130	0.35	171	0.02	108	0.00066	0.37
Oil content:	10	314	0.051	17.9	0.0022	79	0.00044	0.054
45 wt:vol %	15	455	0.074	30.7	0.0035	79	0.00044	0.078
	20	723	0.12	52.5	0.0062	79	0.00044	0.13
	30	1490	0.24	115	0.014	79	0.00044	0.25
	45	3210	0.52	259	0.03	79	0.00044	0.55

\* Calculations are based on a production rate of  $3.0 \times 10^6 \text{ kg y}^{-1}$  ( $360 \text{ kg h}^{-1}$ ).

† Costs are given in US\$ per kilogram of soybean oil product.

‡ Unit electric energy cost: US\$ 0.059 per kWh.

§ Unit cooling water cost: US\$ 4.22 per  $100 \text{ m}^3$ .

# Unit steam cost: US\$ 2.3 per 1000 kg.

the reactor operated at a low current efficiency, large amounts of electric current were required to achieve the specified conversion. The increase in electrical energy resulted in larger cooling water requirements due to more  $I^2R$  heating in the reactor. Since the electrochemical reactors did not require heating, steam consumption (for evaporating water and *t*-butanol from oil) was independent of the applied current density and decreased as the oil content in the electrolyte increased (less solvent was removed for electrolytes with a high oil content). The fact that steam and cooling water requirements were not sizeable contributions to the operating cost was not unexpected; prior economic studies of organic electrochemical processes have shown that operating costs are usually dominated by the reactor's power requirements [17]. Consequently, the lowest manufacturing cost for the oil hydrogenation plant was achieved at the operating conditions that produced the highest current efficiency (i.e., 95% current efficiency at 10 mA cm<sup>-2</sup> and 10 wt:vol % of oil content).

The total production cost of the hydrogenated soybean oil product was determined by adding the capital equipment, equipment installation, and operating costs (where the installation charges were estimated to be 40% of the equipment cost). Figure 7 shows the variations in production cost with current density and oil content for a depreciation period of five years (where equipment depreciation was calculated using a straight line method with zero salvage value). These results show that for any given current density, the lowest total production costs are realized when the oil content in the electrolyte is 10 wt:vol %. Any improvement (lowering) in energy costs for the

separation loop by increasing the oil content of the two-phase reaction medium was offset by the higher electrical power requirements of the reactors due to the drop in both current efficiency and electrolyte conductivity. The lowest production cost (US\$ 0.13 kg<sup>-1</sup>) was obtained at 10 wt:vol % oil and 15 mA cm<sup>-2</sup>. These operating conditions lie between those that minimized capital cost (10 wt:vol % soybean oil/20 mA cm<sup>-2</sup>) and operating cost (10 wt:vol % soybean oil/10 mA cm<sup>-2</sup>). Changing the depreciation period affected the minimum production cost: for example, US\$ 0.18 kg<sup>-1</sup> for a three year depreciation and US\$ 0.10 kg<sup>-1</sup> for a seven year depreciation, but did not alter the current density and oil concentration at the minimum cost.

The oil hydrogenation production cost for the proposed electrocatalytic plant was compared to that for a conventional chemical catalytic hydrogenation scheme. The major unit operations equipment for a batch soybean oil chemical hydrogenation plant included a batch hydrogenation reactor, an external reservoir for the storage of compressed hydrogen gas, a heat exchanger to preheat the oil to the reaction temperature (180 °C), a filter press to remove the nickel catalyst from the oil-catalyst slurry reaction product and the required piping and instrumentation [17]. The catalytic plant was rated for a production capacity of 2500 kilograms of hydrogenated soybean oil per batch. Assuming a daily production of four batches and a working basis of six days per week, the annual capacity for this batch process was equivalent to that of the continuous electrocatalytic process.

As shown in Table 8, the total hydro-oil production cost from the electrocatalytic hydrogenation plant was approximately seven times greater than that from a traditional high temperature chemical catalytic process. The capital cost per kilogram for the separation loop equipment alone in the electrochemical plant is higher than the total production cost for the entire chemical catalytic process. The difference in capital investment for the two plants was due principally to differences in the materials of construction; all equipment in the electrochemical process was made of stainless steel, whereas the catalytic plant was built of mild steel. As a result of the continuous evaporation and condensation of water and *t*-butanol in the electrochemical process, the operating costs in the separation loop were higher than those downstream from the batch chemical catalytic reactor.

Although the economics of the electrochemical oil hydrogenation process as it is currently configured are not encouraging, the quality of the soybean oil product is nutritionally superior to that from a conventional hydro-process (a lower trans isomers content in the electrochemically hydrogenated oil), which could be used to justify a higher consumer price. It is also important to note that the market price for refined soybean oil is approximately US\$ 0.68 per kg [19]. Changing the hydrogenation technology from a chemical catalytic route to an electrochemical process

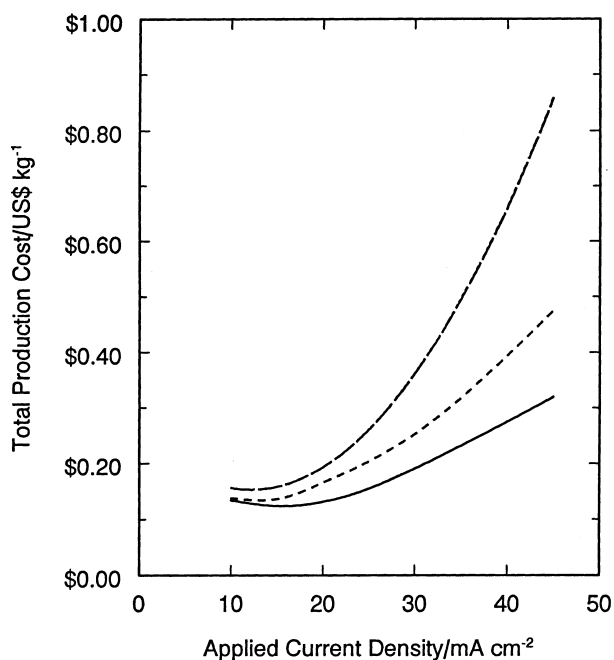


Fig. 7. Total production cost vs the reactor current density and feed stream oil content for a  $3.0 \times 10^6$  kg y<sup>-1</sup> soybean oil electrocatalytic hydrogenation plant. Depreciation period of five years. Electrolyte oil content: (—) 10, (----) 25 and (-·-·-) 45 wt:vol % oil.

Table 8. Comparison of chemical catalytic and electrocatalytic processes for the partial hydrogenation of soybean oil

Utilities and costs	Chemical catalytic process	Electrocatalytic process*	
		Separation loop	Electrochemical reactor system (ERS)
Capital cost, US\$ <sup>†</sup>	165 000	280 000	514 000
Equipment installation cost (US\$) <sup>‡</sup>	66 000	112 000	205 000
Capital + installation cost, (US\$ kg <sup>-1</sup> ) <sup>§</sup>	0.016	0.027	0.049
Steam consumption (kg kg <sup>-1</sup> of oil)	0.23	0.570	0
Steam cost (US\$ kg <sup>-1</sup> )	0.000 44	0.0013	0
Cooling water (m <sup>3</sup> kg <sup>-1</sup> of oil)	0.0037	0.024	0.043
Cooling water cost (US\$ kg <sup>-1</sup> )	0.000 15	0.0010	0.0018
Hydrogen (m <sup>3</sup> kg <sup>-1</sup> of oil) <sup>#</sup>	0.000 990	0	0
Hydrogen cost (US\$ kg <sup>-1</sup> )	0.000 70	0	0
Electrical power, (kWh kg <sup>-1</sup> of oil)	0.033	0.038	0.74
Electric power cost (US\$ kg <sup>-1</sup> )	0.0020	0.0022	0.044
Total operating cost (US\$ kg <sup>-1</sup> )	0.0033	0.0045	0.045
Total production cost (US\$ kg <sup>-1</sup> )	0.019	0.13	

\* Operating conditions: 10 wt:vol % soybean oil and 15 mA cm<sup>-2</sup>.

<sup>†</sup> Includes initial catalyst cost.

<sup>‡</sup> Installation cost: estimated to be 40% of the capital equipment cost.

<sup>§</sup> Depreciation period: 5 years.

<sup>#</sup> Hydrogen cost: US\$ 0.71 m<sup>-3</sup> (Source: Praxair California Inc.).

would increase the raw material + production costs by only 16%. Clearly the production costs for the electrochemical plant are dominated by capital equipment costs. In principle, reactor costs can be reduced by improving the hydrogenation current efficiency at high applied current densities, and by changing the materials of construction (e.g., plastic piping and reactor casings to replace stainless steel). Additionally, the design of the separation loop should be optimized since process equipment accounts for such a large fraction of the total production cost.

## 5. Conclusions

A preliminary process design analysis of a soybean oil electrocatalytic 'brush' hydrogenation plant has been carried out, where the hydro-oil product contained 20% fewer double bonds and the plant capacity was fixed at  $3.0 \times 10^6$  kg y<sup>-1</sup>. The entire analysis was based on a newly developed tubular inward-radial flow-through electrocatalytic reactor containing a packed bed cathode of Raney nickel powder catalyst. Specific accomplishments of this study included: (i) devising a process flowsheet for the reactor network and the unit operations equipment upstream and downstream from the electrochemical reactors, (ii) formulating and testing a semi-empirical porous electrode model in order to reproduce the experimentally observed variation in oil hydrogenation current efficiency with changing current density and electrolyte oil content, (iii) linking the Fortran computer code for the porous electrode flow reactor

model to the commercially available PRO/II heat and mass balance software, (iv) performing capital and operating cost analyses of the oil hydrogenation plant based on the results of the PRO/II simulator, and (v) identifying the optimum conditions for operating the electrochemical reactors (within the range of conditions examined experimentally with a laboratory-scale reactor) that minimized the sum of capital and operating costs for the entire plant. The PRO/II computer design/heat balance/mass balance program for the oil hydrogenation plant can easily accommodate a more sophisticated computer program for the cathode component of an electrocatalytic hydrogenation reactor (such as the glucose-to-sorbitol electrohydrogenation flow cell model developed by Anantharaman and Pintauro [20]) or simple algebraic correlations of the variation in oil hydrogenation current efficiency and cathode overpotential with the applied constant current density and the oil content of the electrolytic solution. Based on the PRO/II simulation results, the total production cost for a brush hydrogenation oil product would be lowest at a current density of 15 mA cm<sup>-2</sup> and a feed composition of 10 wt:vol % soybean oil in solvent/supporting electrolyte (US\$ 0.13 kg<sup>-1</sup> for an assumed five year straight line depreciation of capital equipment). This cost was found to be higher than that for a comparable-size chemical catalytic soybean oil hydrogenation plant (US\$ 0.019 kg<sup>-1</sup>). When the cost of the soybean oil starting material (US\$ 0.68 kg<sup>-1</sup>) was factored into the economic analysis, the production plus raw material cost of the electrocatalytic process was only 16% greater than that for the chemical

catalytic plant. The higher production cost for the electrosynthesized hydro-oil product may be tolerable in the consumer marketplace because the oil has a high nutritional value (a lower *trans* isomers content) and may command a higher selling price.

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