Sunflower Oil Hydrogenation on Pd/C in SC Propane in a Continuous Recycle Reactor

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Fluid-phase, continuous hydrogenations of sunflower oil on 2% Pd/C were carried out in an internal recycle, radial-flow, packed-bed microreactor (50 cm^3) using propane as supercritical-fluid solvent. Temperature (428–488 K), oil liquid hourly space velocity (LHSV = 30–70), H_2 mol composition (2–10%), and stirrer speed (52–262 rad/s) were changed according to a four-variable, two-level, central composite design to predict the effect of process variables on the iodine value (IV) and on trans fatty acid content (trans C18:1). Feed and product were well above the condensation conditions so that a single fluid phase was present (according to recent calculations by Pereda et al.). The total system pressure, the molar oil concentration and the catalyst mass were held constant at 20 MPa, 1 mol %, and 0.1085 g, respectively. An empirical quadratic-form response-surface model is shown to fit the results, and shows the regions where a potential CSTR process could be operated to obtain a certain outlet iodine value and a minimum trans C18:1 content. For the time-on stream values used here catalyst deactivation effects were not observed. In an extension of the results, a kinetic analysis of the steady-state CSTR reaction rate data allows determination of the kinetic constants, and their temperature dependency, for the multiple reactions of hydrogenation–isomerization network involving triglyceride species. The kinetic formalism, proposed earlier for vegetable oil hydrogenations, was used. *AIChE J,* 50: 1545–1555, 2004

Keywords: hydrogenation, vegetable oil, supercritical fluid solvents, phase equilibria, experimental central composite design, response-surface methodology kinetics on Pd catalyst

Introduction

Hydrogenation of vegetable oil is an important process in the food industry because of its widespread application to produce margarines, shortenings, and other food components. In the hydrogenation process, unsaturated fatty acid chains of triglycerides are partly reacted with hydrogen in the presence of a porous catalyst, according to the reactions shown Figure 1 (Wisniak and Albright, 1961). A saturated chain thus increases the stability of fat to oxidative rancidity and converts liquid oils to a semisolid form, mostly for further use in certain food applications. The physical and sensory properties of the final product strongly depend on the number of residual double bonds as well as on the contents of *cis–trans* isomers present in the mixture.

In the conventional slurry process, the performance of the batch multiphase reactors at low hydrogen pressure (<0.5 MPa) and high temperatures (383–443 K), with a nickel-based catalyst, presents problems of H_2 availability attributed to the low solubility of hydrogen in organic liquids, as well as interface mass transport limitations (Härröd et al., 1997). These two factors decrease the effective H_2 concentration in the liquid and on the catalyst particle, thus limiting the global reaction rate and promoting the unwanted isomerization of *cis* double bonds

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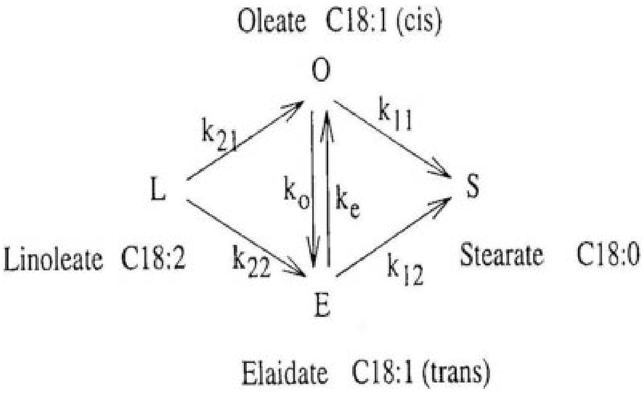

Figure 1. Accepted triglyceride interconversion during hydrogenation of vegetable oils (H_2 not shown; Wisniak and Albright, 1961).

to the *trans* configuration. On the other hand, the hydrogenation is a highly exothermic reaction so that temperature control is essential (see Farrauto and Bartholomew, 2000; Satterfield, 1996).

Somewhat conflicting conclusions have resulted from studies on the *trans* fatty acids. These isomers formed during hydrogenation of fatty oils have been shown to have similar effects in the human body as saturated fats. Today, recognized human health and food organizations are recommending a reduction in *trans* fatty acid esters in the diet, which suggests using oils that have preferably been hydrogenated only slightly (Rase, 2000). Thus low *trans* C18:1 content is a desirable objective with respect to food health.

The recent interest in the use of supercritical (SC) fluids as reaction media is associated with their solvent power under reaction conditions and their performance as solvents for rapid mass and heat transfer (Savage et al., 1995). On the other hand, SC carbon dioxide is already considered the solvent of choice for green chemical processing (Beckman, 2003). In the case of hydrogenation, the SC fluid is used to dissolve all the reactants (oil triglycerides and H_2) and form a single, homogeneous vapor phase, in which the mass transport resistance problem is alleviated. With respect to the reactants, their concentrations on the catalyst can be varied in a more flexible manner and not dictated by the unfavorable equilibrium solubility, as in the case for H_2 in multiphase reacting systems. In this way, higher reaction rates can be reached and the amount of unwanted byproducts can be reduced to obtain a higher product quality. Poliakoff and coworkers (1998) reported on the unique ability of SC solvents to change selectivity in quite a large number of organic processes.

Tacke et al. (1996, 1997) reported full or partial hydrogenation of fats and oils, fatty acids, and fatty acid esters using near-critical and supercritical CO_2 and/or propane mixtures at temperatures between 333 and 393 K at a total pressure up to 10 MPa. The reactions were conducted in a continuous fixed-bed reactor with palladium (Pd) on Deloxan as proprietary catalyst. The authors observed significantly improved space–time yields compared to those of hydrogenation in other types of reactors (such as conventional trickle bed and slurry), a longer catalyst life, and a higher selectivity.

Similarly, Härröd and coworkers (1996, 1997, 1999) investigated the hydrogenation of fatty acid methyl esters (FAMEs) and oils, noting very high reaction rates and reduced byproduct formation in a fixed-bed reactor operating with a single fluid phase. High reaction rates were explained in terms of the higher hydrogen concentration external to the catalyst particle, compared to that in a two-phase reaction. They further note that faster hydrogen transfer rates could also play a role.

In a recent review, Ramírez et al. (2002) recently systematized the data of several authors regarding hydrogenation rates. They observed cases where the SC solvent brings about reaction rates 300 times higher than those observed in a conventional Pd/Al_2O_3 slurry reactor or a trickle bed (Smith, 1981).

Macher and Holmqvist (2001) carried out the hydrogenation of palm oil in near-critical and supercritical propane using a small (0.5 cm^3) continuous fixed reactor and 1% Pd/C as catalyst, temperature (338–408 K), H_2/triglyceride mol ratio (4–50), and residence time (0.2–2 s) to assess the iodine value (IV) as a function of the operating variables. The authors observed high reaction rates (a residence time of 2 s is sufficient at 393 K), which indicates that the reaction could also be run successfully at lower temperatures.

King et al. (2001) studied the hydrogenation of soybean oil using pure hydrogen mixed with SC CO_2 at 14 MPa and 393–413 K, in a conventional nickel catalyst in a slurry reactor. They found that at constant temperature, the mixture of SC $CO_2 + H_2$ exhibits a slower reaction rate than that using pure hydrogen, and that reaction conditions had a strong influence on the characteristics of the final product.

In a previous work, Ramírez and Larrayoz (2002) presented preliminary experimental data from a continuous, single-phase hydrogenation of sunflower oil on Pd/C carried out in a Robinson-Mahoney–type of reactor, with a fixed bed catalyst using propane as SC solvent. The results showed that it is possible to predict the formation of several hydrogenation products with certain characteristics for different industrial applications by changing the operating conditions, given that the final product distribution depends on temperature, pressure, and feed mixture composition.

In the present study, we carried out the hydrogenation in propane, as in a one-phase supercritical mixture, at conditions well above the two-phase region to avoid condensation using a well-mixed, Pd/C catalytic, radial flow packed-bed reactor, with internal recycle. We studied how the operational variables affect the sunflower hydrogenation process to assess both the reduction in iodine value and the formation of *trans* C18:1 isomer, parameters that are necessary for further industrial food application. We approached the design problem using an empirical response-surface methodology. Furthermore, formal kinetic analysis of the reactor data allowed us to establish the kinetic scheme for the multiple reaction network.

Hydrogenation Reactor Setup

Raw materials

A sunflower seed oil from *Helianthus annuus* from Sigma-Aldrich (Barcelona, Spain) that had an initial iodine value (IV) of 130 and a fatty acid composition [13.2% saturated (C16:0, C18:0), 18.4% *cis* C18:1, 67.6% C18:2, and 0.8% C18:3] was used in all experiments. Propane (99.5% minimum purity

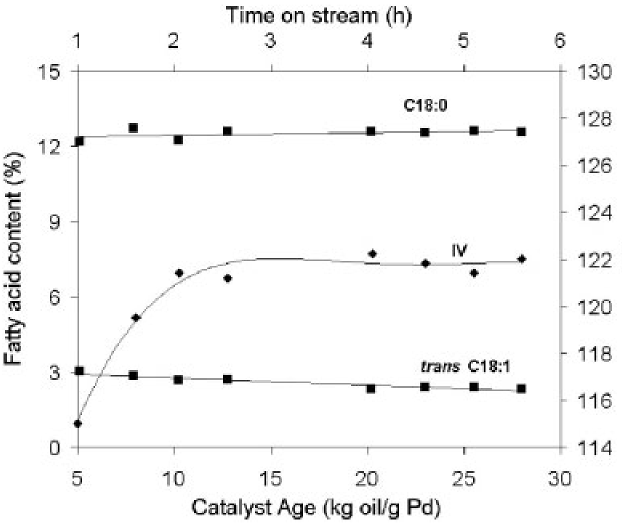

Figure 2. Change in product distribution and iodine value (IV) during short term operation of a hydrogenation reactor (*P* = 20 MPa *T* = 444 K, feed mol composition: sunflower oil = 1%, H_2 = 8%, propane= 91%).

grade) and hydrogen (99.999% minimum purity grade) were purchased from Praxair (Barcelona, Spain).

The catalyst used was 2% Pd on activated C (uniform metal loading; 2 mm pellets; surface area = 1530 m^2/g; pore volume = 1.3 cm^3/g, mostly in micropores; and bulk density = 360 kg/m^3), from Degussa AG (Frankfurt, Germany). Before the hydrogenation, catalyst pellets were crushed and sieved to 0.55 mm and then the powder was activated in situ by flushing N_2 (99.999% minimum purity grade) into the reactor to remove oxygen and then displacing nitrogen with pure hydrogen (105 STP cm^3/min) at high pressure and temperature for 2 h.

Hydrogenation runs (duration of about 5 h) were done after the catalyst activity had become stable (see Figure 2). Conversion in terms of IV, *trans* C18:1 content, and stearic ester content showed an initial decrease, but were stable during reaction runs.

Equipment

Hydrogenation runs were carried out in an internal recycle, gradientless microreactor (Robinson, 1986), with the catalyst held in an annular basket made of mesh screens. Recycle flow was delivered by a variable-speed stirring-shaft, pumping radially through the bed. To avoid reactor-wall effects the vessel was fabricated from a nickel-free, alloy bar (holding a free volume of 50 cm^3). Blank runs showed no catalysis by the wall. Because of the large fan speeds used (up to 105 rad/s), well-mixed conditions prevailed. The experimental reactor setup is shown in Figure 3.

Liquefied propane was pumped using a high-pressure diaphragm pump (Milroyal® D, Dosapro Milton Roy, France) to the reactor, to provide and maintain a system downstream pressure of 18–25 MPa, which was manually set with a high-pressure regulator (Model PR57, GO, Euroval, Barcelona, Spain). The sunflower oil was pumped at a constant flow rate

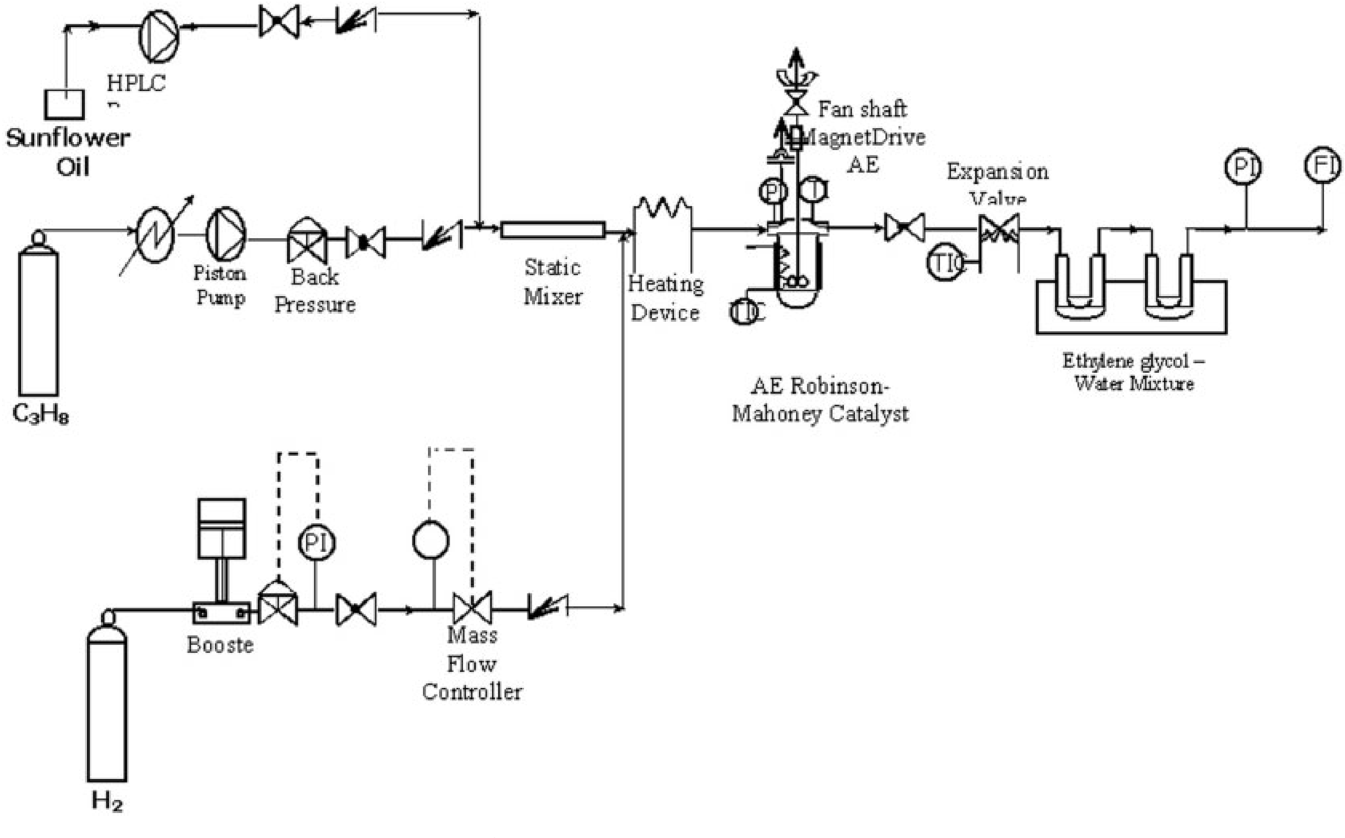

Figure 3. Continuous hydrogenation reactor setup.

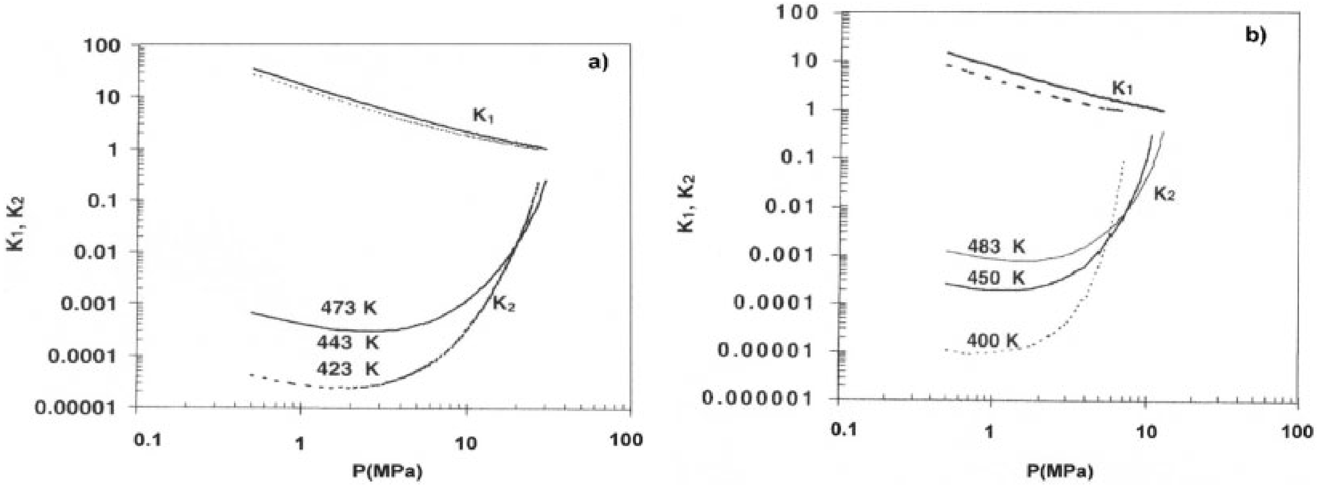

Figure 4. VLE in binary systems. Sunflower (K_1) and SC fluid solvent (K_2) VLE constants vs. pressure at constant temperature: (a) in carbon dioxide; (b) in propane.

using a high-performance liquid chromatography (HPLC) pump (Gilson 305, France) and H_2 was compressed by a gas-booster system (AG-62, Haskel, Barcelona, Spain) equipped with a high-pressure gas reservoir. H_2 flow was metered from the constant pressure reservoir through a mass-flow–indicating controller (Model 5850S, Brooks Instruments, Euroval, Barcelona, Spain).

The oil substrate was mixed with propane in a 20-cm long, 1/4-in. OD, static mixer (37-04-065, Kenics, Barcelona, Spain). H_2 was added downstream of mixer. The reactant mixture was preheated to the desired operating temperature before entering the reactor. The reactor (Robinson-Mahoney reactor, Autoclave Engineers, Erie, PA) was equipped with a fan shaft (MagneDrive, Autoclave Engineers), which created a flow through the basket to the reactor wall for upward/downward deflection and a fixed annular catalyst basket (52 × 52 mesh, catalyst volume = 8.6 cm^3), which had baffles inside and outside the basket to prevent vortexing. The reactor was heated with an electrical heating jacket. Control thermocouples were located in the outside skin of the reactor body. The internal reactor temperature was monitored with a thermowell located in the bottom. The temperature increment in the reactor, relative to the feed, was seldom more than 274.15 K above the temperature of the inlet heater. This is certainly attributed to the relatively small adiabatic temperature increase for reactions in SCF solvents.

After leaving the reactor, the effluent was continuously expanded to atmospheric pressure on an externally heated needle valve to control the total flow of the reactor mixture. This effluent was then sent to a series of glass U-tubes, immersed in an ethylene glycol–water (40% v/v) bath held at 249 K to condense the oil from the propane and unreacted H_2 mixture. The flow rate of exhaust gas was measured with a rotameter (Model 2300, Tecfluid, Spain) and sent to an explosion-proof absorption system.

Analytical methods

Catalytic hydrogenation rates were calculated by measuring the decrease in IV using the Wijs titration method (1988). Fatty acid compositions of the resultant products were determined on a 250 × 4.6 mm, silver-ion column (Chromspher 5 lipids CP28313, Varian, Madrid, Spain) in an HPLC system (2410, Waters, Spain) using the isocratic method (Adlof, 1994). The HPLC analysis was performed on the methyl ester form of the triglyceride samples. Methyl esters were prepared by the method described in the French Standard (NF T 60-233, 1977). The elution solvent was heptane/acetonitrile 99.7:0.3% v/v (both HPLC grade from Panreac, Spain). The advantage of the HPLC method over the GC method is that it allows a more complete separation of the *cis* and *trans* C18:1 isomers (López, 2002). Occasionally melting points of products were occasionally determined using differential scanning calorimetry (Piris 1 DSC Perkin-Elmer, Spain).

Achieving One-Phase Fluid Mixture

To ensure a single-phase vapor phase, the operating pressure and temperature for the reactor were held above the mixture critical values estimated with the Chueh–Prausnitz (Reid et al., 1987) approximation. For a typical reacting mixture (composition in wt. % as: H_2 = 9%, oil = 1%, C_3H_8 = 90%), the critical values are T_c = 389 K and P_c = 6.2 MPa.

The binary vapor–liquid equilibrium (VLE) diagrams for sunflower oil in CO_2 and propane are shown in terms of the VLE constants as a function of pressure at constant temperature in Figures 4a and b and were published in a previous review (Ramírez et al., 2002). These were calculated for the system C_3H_8–sunflower oil, estimating the K_i values from the fugacity coefficients calculated with the PR-EOS (McHugh and Krukonis, 1994; Sandler, 1999). The calculations were performed with a PE 2000 (Pfohl et al., 2000) in terms of the convergence pressure (Hougen et al., 1954). Although these are approximate ($k_{12} \sim 0$, $l_{12} \sim 0$, were assumed), the propane–oil binary mixture has a convergence pressure of around 14 MPa, whereas the system with CO_2 instead of C_3H_8 has a convergence pressure of around 33 MPa (Ramírez et al., 2002), significantly above that for the propane–oil system. Therefore, with respect to the reactor operating pressure, it would be less expensive to use propane rather than carbon dioxide. Recently,

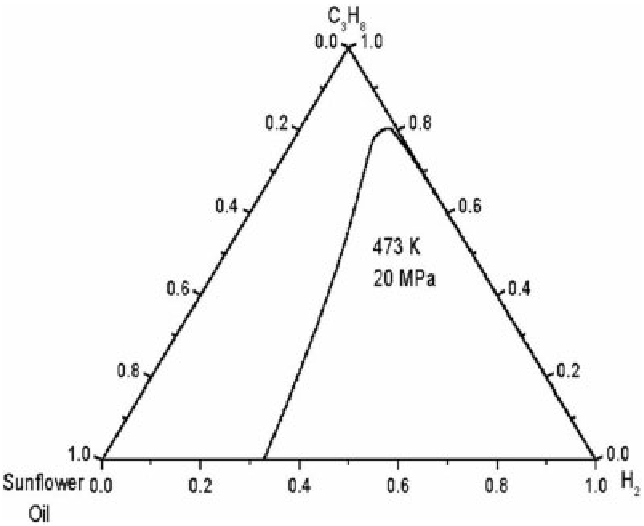

Figure 5. Propane–H_2–sunflower oil ternary system estimated with the Peng–Robinson EOS (see Sandler, 1999) at 473 K and 20 MPa in mol % (Sans, 2003).

Pereda et al. (2003) and Sans (2003), for the same reacting system (sunflower oil, H_2, and SC propane as solvent), described ternary phase equilibria using the GCA-EOS to calculate the single-phase boundaries for the reacting mixtures for hydrogenations in supercritical fluids. They derived a general expression relating the required propane fraction, to have the vegetable oils in a single vapor phase in terms of the mol oil/mol H_2 stoichiometric ratio in the reactor feed. The phase diagram for the ternary system, calculated up to 473 K and 20 MPa in triangular form, is shown in Figure 5.

In our experiments, noncondensing conditions were monitored by watching the increase in pressure drop across the reactor in the same way as reported by Van den Hark and Härröd (2001). We observed that one-phase equilibrium conditions are theoretically met but the system requires a finite or longer contact time to reach fluid uniformity. This was observed in some of the initial runs where it seemed that condensation had occurred. The use of an online static mixer helped to achieve the solubility by using 20 cm of mixer length.

Experimental Strategy and Modeling

We next describe how we used empirical modeling to determine practical ranges of reaction variables, using experimental design concepts, with the objective of obtaining low % *trans* isomer for a moderate IV reduction. Based on the above phase-equilibrium considerations, the ranges of operating conditions (see Table 1) were selected to avoid condensation.

Table 1. Statistical Upper and Lower Experimental Levels for Reaction Variables

Process Variables	Low Level (−1)	High Level (+1)
Reaction temperature, K	443	473
Liquid hourly space velocity (LHSV), h^{-1}	40	60
H_2, mol %	4	8
Reactor stirrer speed, rad/s	105	209

Table 2. Coded 2^4 Factorial Design Matrix

Run	Temperature	LHSV	%H_2	Fan Speed
1	−1	−1	−1	−1
2	1	−1	−1	−1
3	−1	1	−1	−1
4	1	1	−1	−1
5	−1	−1	1	−1
6	1	−1	1	−1
7	−1	1	1	−1
8	1	1	1	−1
9	−1	−1	−1	1
10	1	−1	−1	1
11	−1	1	−1	1
12	1	1	−1	1
13	−1	−1	1	1
14	1	−1	1	1
15	−1	1	1	1
16	1	1	1	1

The total system pressure, the molar oil concentration, and the catalyst mass were kept constant at 20 MPa, 1 mol %, and 0.1085 g, respectively.

To achieve uniformity for the above conditions, it is required to have 8 kg propane/kg oil fed, according to the calculations of Pereda et al. (2003). The values used here (12–15 kg/kg) are substantially higher. From an experimental viewpoint undue phase separation was unobserved, in agreement with the calculations and with the ternary system calculations.

To evaluate the effect of the process variables and their interactions on the hydrogenation reaction, the following second-order polynomial model (Box et al., 1978) was used:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \sum \beta_{ij} x_i x_j + \in \quad (1)$$

This expression describes the correlations between the significant predictor reaction variables (x_i) and the predicted responses (y).

The experiments, at different operating conditions, were carried out according to a four-variable, two-level, central composite design [2^4 factorial design + 8 star points (SP) + 1 center point (CP) = 25 experiments]. The coded experimental design matrix is shown in Table 2 and Table 3. The observed responses were the iodine value (proportional to conversion) and *trans* C18:1 (indication of selectivity). A lined out activity catalyst was used. The calculations were done using the statistical software package MINITAB (Applegate and Minitab, 1996).

Table 3. Coded Center (CP) and Star Points (SP) Design Matrix

Run	Temperature	LHSV	%H_2	Fan Speed
17 (CP)	0	0	0	0
18 (SP)	−2	0	0	0
19 (SP)	2	0	0	0
20 (SP)	0	−2	0	0
21 (SP)	0	2	0	0
22 (SP)	0	0	−2	0
23 (SP)	0	0	2	0
24 (SP)	0	0	0	−2
25 (SP)	0	0	0	2

Table 4. Effects of the Increase Either in the Temperature, the LHSV, or the $\%H_2$ for the Mean Values of the Other Variables

Run	IV	*trans,* wt %
17	117.6	2.3
18	120.3	1.1
19	95.17	4.6
20	113.1	2.4
21	119.4	2.1
22	121.3	2.2
23	110.7	3.1

After collecting response data, the experimental factors that have substantial effects on the reaction were determined using the *p*-values (which represent the probability of rejecting nonsignificant experimental variables) of the estimated effects and the table of coefficients for the initial regression from the experimental results. Then, the second-order polynomial models were constructed.

The significance of the results is indicated by the estimated standard deviations (*s*) of the model, which is used as a measure of dispersion.

Results and Discussion

The collected response data were fit to a full mathematical model using MINITAB® software, which includes the four main factors [$\%H_2$, LHSV, *T*, fan (or stirrer) speed], six two-way interactions, and four quadratic-way interactions.

Using the values in the *p*-factor (<0.05), we determined the factors that were significant for the responses under study (IV and *trans* content). Thus it is observed that the main effect was attributed to *T*. The LHSV–$\%H_2$ interaction and *T*–$\%H_2$ interaction came next and were more important than the effects of LHSV or $\%H_2$ alone. The fan speed was the least important factor.

The estimated standard deviations (*s*) of each final polynomial regression models ($s = 6$ for the iodine value (IV) and $s = 0.73$ for the *trans* C18:1 content) were considered to be low. These deviations were attributed mainly to some experimental instabilities in the flow rate (such as fluctuations in the gas feed flow rates) or to analytical variability (lack of precision) problems.

An increase in either the temperature, the residence time, or the $\%H_2$ (for the mean values of the other variables) involves an increase in conversion and in the *trans* acid content (see experiments 17–23 in Table 4). Although the response of conversion is as expected, the effect of $\%H_2$ on the *trans* content is opposite to what is observed in the low-pressure vegetable hydrogenations (Farrauto and Bartholomew, 2000). On the other hand, if the temperature alone is increased, although more hydrogen is supplied to the catalyst surface, the reaction is very rapid and the hydrogen on the catalyst may be partially depleted. This would account for the increased isomerization at higher temperatures. There is not enough hydrogen on the catalyst surface to complete the saturation, so the catalyst takes back hydrogen and a *cis–trans* isomeric double bond results (Hui, 1996). This same thing happens in the low-pressure hydrogenation process.

For other values of the operating variables, the effect of temperature is not as clear because of the interactions between variables. That is, the effect of one variable on the response of interest depends on the values taken by the other variables. For example, at high temperature, an increase of $\%H_2$ causes a decrease in % *trans*, for any LHSV, whereas the observed effect is the opposite at low temperature. When LHSV is increased (for any $\%H_2$) the same behavior is observed depending on the value of temperature. If the temperature is low, the % *trans* increases and if the temperature is high, the *trans* content decreases (see Figures 6a and b). For short contact times (high LHSV), an increase in temperature decreases the *trans* content (for $\%H_2 < 6\%$), whereas for low LHSV the opposite effect is observed, irrespective of $\%H_2$ in the feed.

Quite surprisingly, it is observed that at high space velocities, an increase in temperature or H_2 concentration causes greater hydrogenation extension than that at low space velocities. This is seen in Figures 7a and b, respectively. Kinetically, this is not the expected behavior. A possible explanation is that for low LHSV an increase in H_2 produces a decrease in

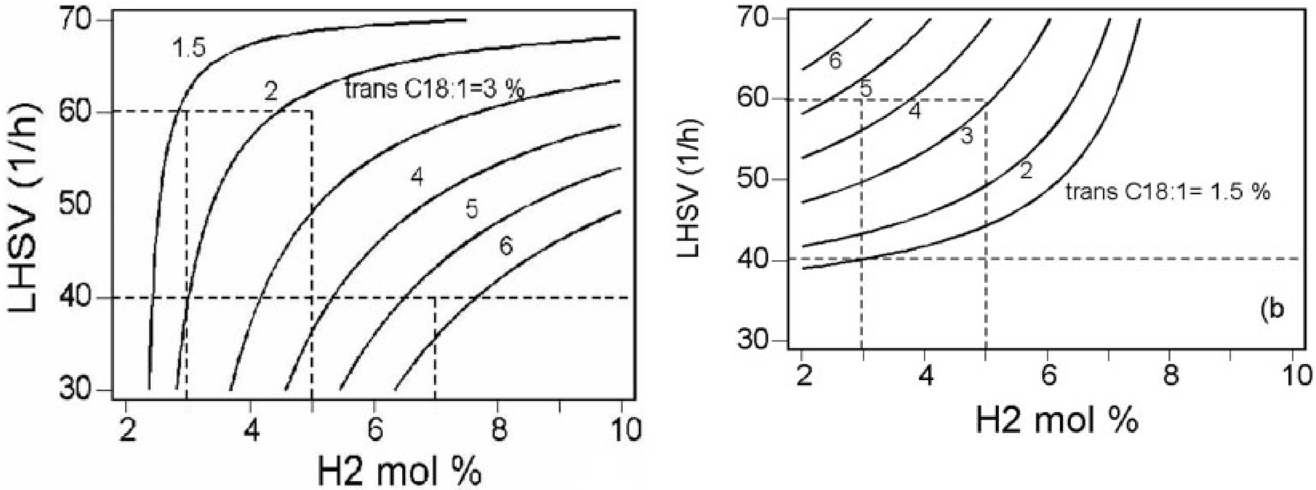

Figure 6. Contour map based on empirical quadratic model. High fan speed: (a) LHSV vs. $\%H_2$ at 488 K; (b) LHSV vs. $\%H_2$ at 428 K.

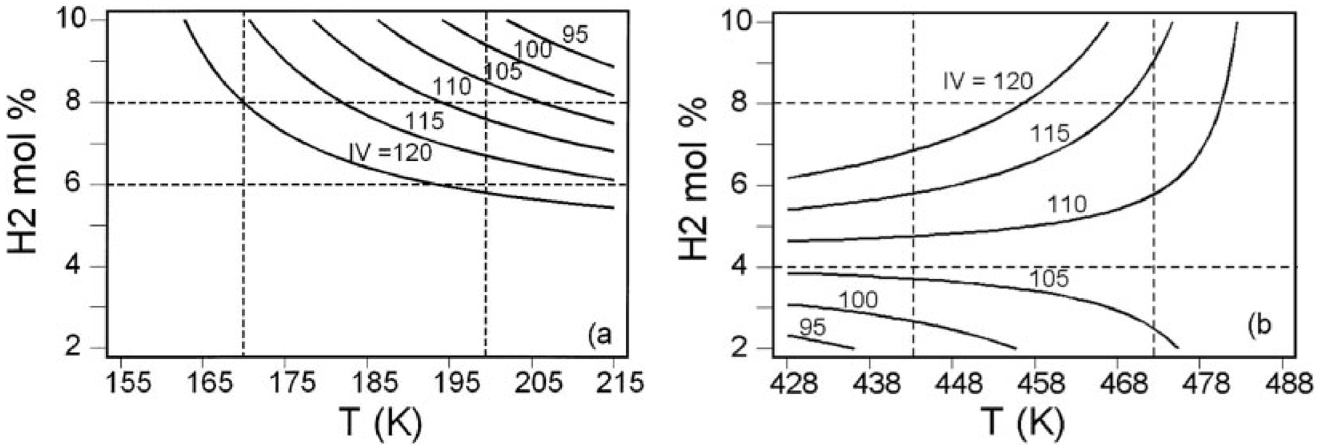

Figure 7. Contour map based on empirical quadratic model. High fan speed: (a) $\%H_2$ vs. T at LHSV = 70 h^{-1}; (b) $\%H_2$ vs. T at LHSV = 30 h^{-1}.

solubility of oil in the reaction medium, which brings about some condensation in the catalyst pores, thus increasing internal mass transfer resistance.

The effect of the recycle rate was also considered in the design. An increase in operating fan speed from 52 to 262 rad/s produces a slight increase in rate (higher conversion). The effect of stirring speed on the *trans* content is similar to that on the IV. The physical effect of increasing fan speed on *trans* content is consistent with the effect of removing some of the diffusional resistance in a net of multiple reactions (Smith, 1981), which improves the yield in middle products. Even though the rate in the present reactor is small, its effect cannot be overlooked in a packed bed reactor without recycle and with larger size of catalyst, particularly if very low *trans* isomer is wanted in industrial production.

Reactor operating conditions

From the study of the operating variables on IV reduction and *trans* content and their interactions, it is possible to derive different sets of reaction conditions leading to increased conversion while at the same time lowering the *trans* C18:1 isomer content. So in principle one set of possible reaction conditions would be to operate the reactor on the high-temperature range and high $\%H_2$ range together with a high space velocity (LHSV). By contrast, a second combination would be to use low LHSV, low T, and $\%H_2 < 4\%$. There are other possibilities as well.

In practice, a final hydrogenation product can be obtained that exhibits a low *trans* C18:1 at conversion by allowing some increase in the content of saturates (in the form of stearic chains) or by having a low degree of monounsaturates. In the former case, the final product could have suitable plastic properties, but could be objectionable with respect to health. In the second case, the necessary plasticity would not be suitable for other applications.

From results of this study, it is possible to determine the optimum operating conditions to obtain a final hydrogenated product of immediate food application (such as for margarine/shortenings production), such that it has a low *trans* content ($<3\%$) and a moderate IV reduction (final $90 < \mathrm{IV} < 110$) together with a relatively low stearic content ($<20\%$). Figures 8a and b show different alternative operating conditions (clear colored) that simultaneously fulfill the above specifications. For example, a good combination of operating conditions would be on the upper settings of the variables (T = 473 K, LHSV = 60 h^{-1}, H_2 = 9%, fan speed = 262 rad/s), among other possibilities, as shown in Figures 8a and 8b.

Some of the experimental results are presented in Figures 9 and 10, together with typical data corresponding to the conventional low-pressure process, as well as the results reported by King et al. (2001) for the hydrogenation of soybean oil in a high-pressure, slurry reactor with SC CO_2 and H_2.

It is seen that for the same degree of hydrogenation, the % *trans* obtained in the runs is substantially lower than that obtained in the conventional process and that reported by King et al., whereas the stearic ester content (expressed as % newly formed stearic based on initial stearic in feed) is slightly larger than that obtained in the conventional process, and quite similar to that published by King et al. (2001).

Table 5 shows the characteristics of the commercial raw materials used in margarines and shortenings, together with the experimental results of King et al. as well as the results obtained in the present work. It is worth mentioning the great potential of SC hydrogenation compared with the conventional process because it allows using a final product with the required plasticity as well as a low % *trans* value by properly choosing reaction conditions.

Kinetic Analysis of CSTR Data

The experimental design approach presented also allows the calculation of the main kinetic parameters, provided that kinetic expressions are assumed for the reactions of Figure 1. On the other hand, as seen in the experiments, fluid-to-particle mass-transfer resistance is not significant, and the particle size of the catalyst was small. Therefore, observed rates can be taken as intrinsic catalytic rates free from diffusional effects. For this purpose, internal recycle reactors are well suited.

Mechanistic kinetic models for the hydrogenation–isomerization reaction network of Figure 1 are available for vegetable triglycerides on either Raney-type or supported nickel. For supported Pd or Ni catalysts studies are more recent (for example,

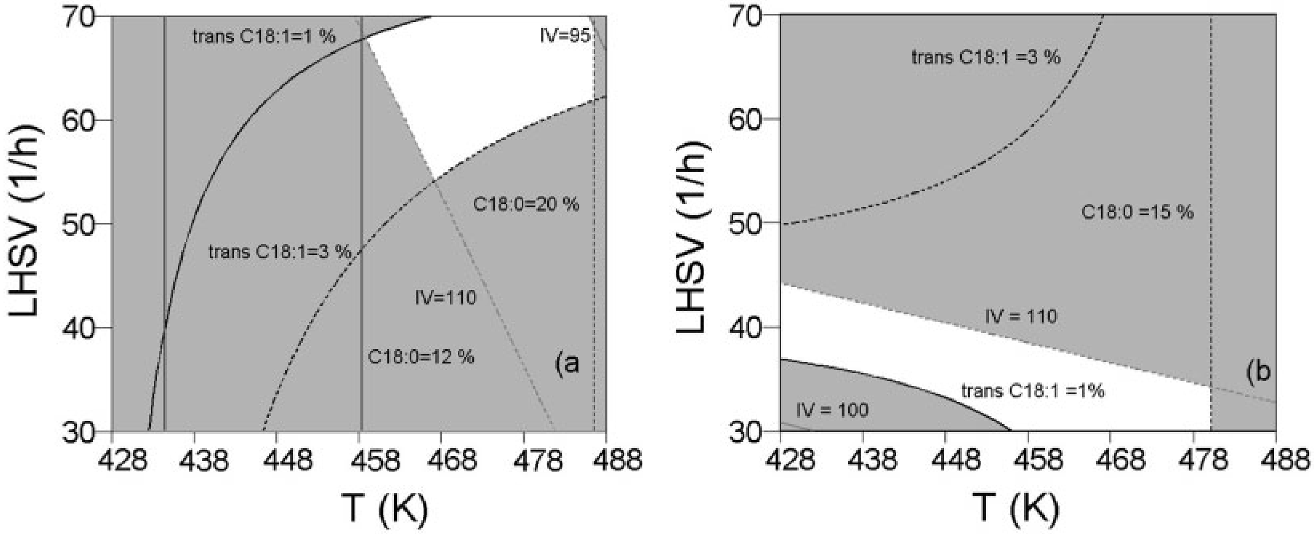

Figure 8. Operating zones in the LHSV–*T* plane (a) in the high H_2 composition range between *trans* = 1 and 3%, for IV = 95–110, and stearic ester = 12–20%; (b) in the low H_2 composition range.

Fillion et al, 2000; Santacesaria et al., 1994). The important feature is that hydrogenation and isomerization take place on the same sites, given that monounsaturate adsorption plays a key role in both reactions. It is accepted that hydrogenation occurs by reaction of adsorbed atomic hydrogen next to a linoleic ester adsorbed on an adjacent site. The controlling mechanism is the surface reaction between adsorbed esters (L, O, or E) and adsorbed hydrogen atoms; therefore reactions are half order in the

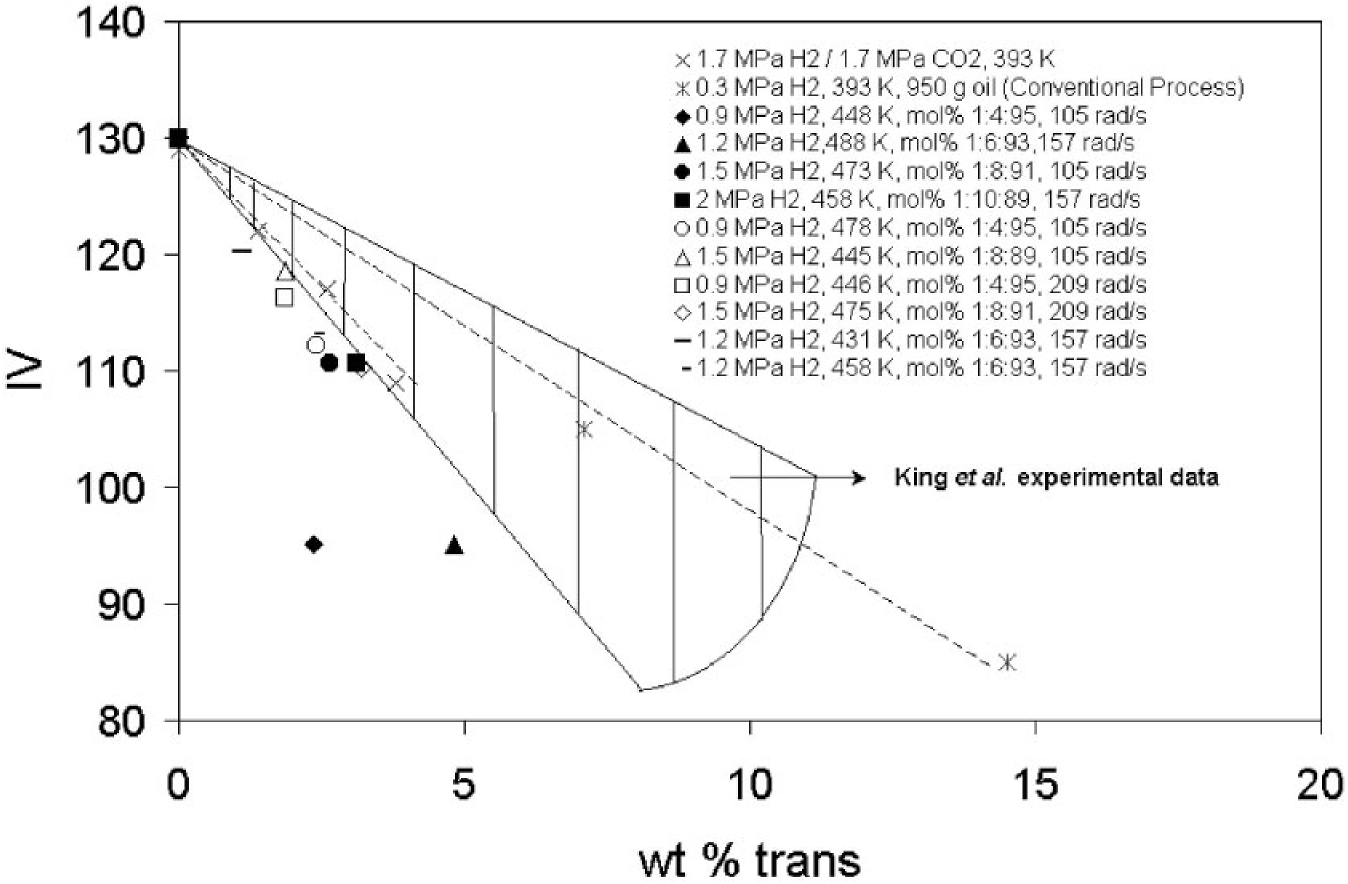

Figure 9. *trans* C18:1 formed vs. reduction in IV in continuous hydrogenation of sunflower oil on Pd. Initial IV = 130. Data by King et al. (2001) lie within dashed region.

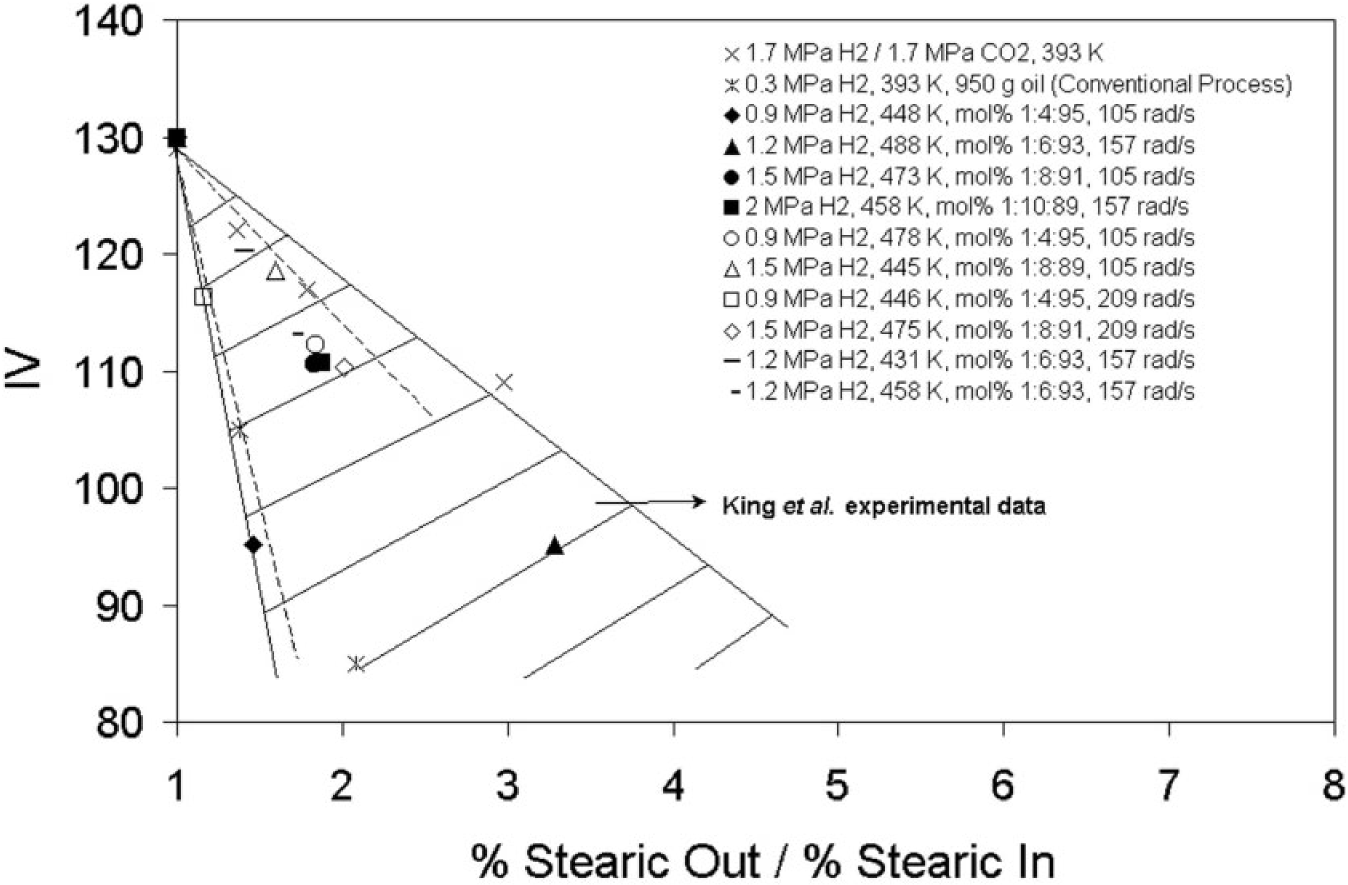

Figure 10. Stearic ester formed vs. reduction in IV in continuous hydrogenation of sunflower oil on Pd; initial IV = 130. Data by King et al. (2001) lie within dashed region.

dissociating species (Smith, 1981). *Cis–trans* isomerization takes place through the hydrogenation to a saturated intermediate, and thus is also expected to be half order in H_2.

The above features have been put in terms of fluid phase concentrations for the case of cottonseed oil hydrogenation (Hashimoto et al., 1971) as follows

$$r_L = -(k_{21} + k_{22}) C_L \sqrt{C_{H_2}} \tag{2}$$

$$r_O = k_{21} C_L \sqrt{C_{H_2}} - k_O C_O \sqrt{C_{H_2}} + k_E C_E \sqrt{C_{H_2}} - k_{11} C_O C_{H_2} \tag{3}$$

$$r_E = k_{22} C_L \sqrt{C_{H_2}} + k_O C_O \sqrt{C_{H_2}} - k_E C_E \sqrt{C_{H_2}} - k_{12} C_O C_{H_2} \tag{4}$$

Table 5. Partially Hydrogenated Vegetable Oils vs. Commercial Margarine Basestocks (DP 305–312 K): Data on Iodine Value, *trans* Content, and Stearic Production

Process	IV	*trans*, wt %	% C18:0 Out/ % C18:0 In	Substrate
Conventional process	90–110	11–30	1.4–2.1	Soybean oil
King et al. (2001)*	108–114	2.5–5	1.7–2.6	Soybean oil
Present study (SC propane)	95–110	2–5	1–3.3	Sunflower oil

*Experimental SC conditions: 393 K, 0.02 wt % Ni catalyst, 1.7 MPa H_2 + 1.7 MPa CO_2.

$$r_S = k_{11} C_O C_{H_2} + k_{12} C_E C_{H_2} \tag{5}$$

$$r_{H_2} = -3k_{21} C_L \sqrt{C_{H_2}} - 3k_{22} C_L \sqrt{C_{H_2}} - 3k_{11} C_O C_{H_2} - 3k_{12} C_O C_{H_2} \tag{6}$$

in which an order 1/2 with respect to hydrogen was considered for the reactions involving di- and monounsaturates (Figure 1), and first order for the formation of stearic ester from oleic or elaidic esters.

The last equation gives the total hydrogen uptake rate. Note that for low concentrations of monounsaturates (O and E) and large concentrations of linoleic ester (L), the last two terms will be small, and thus the overall H_2 consumption rate will be half order in H_2 and proportional to CL. The half-order is observed in Figure 11, where log rate data, as a function of log hydrogen partial pressure, are shown. The bottom line corresponds to 448 K. The slope of the regression line is 0.48, very near to the theoretical value 0.5. The upper line corresponds to a higher temperature (460 K) both for 262 rad/s and 20 MPa. The slope for the upper line is 0.52. These results suggest an order 1/2 with respect to hydrogen concentration, so it lends some confidence on the kinetic formulation given above.

Given the above kinetic scheme it is possible to fit the kinetic constants for the multiple reaction system as follows. The

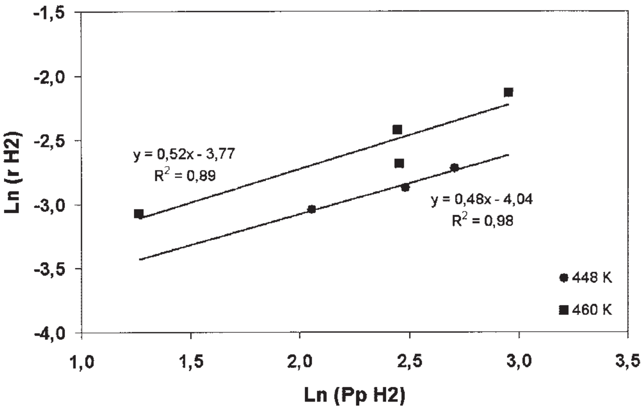

Figure 11. Linearized plot of hydrogen uptake rate: ln(rH_2) vs. ln(pH_2), for 448 and 460 K. Upper line slope = 0.52; bottom line slope = 0.48.

steady-state conservation equations for multiple reactions in a CSTR is given by the system of equations:

$$F_{i0} - F_i + r_i W = 0 \qquad i = 1, 5 \tag{7}$$

where W is the mass of catalyst in the CSTR and r_i is the global rate of formation for species i. Substitution of the rate expressions given before in the balance equations provides a system of equations in the concentrations and in terms of parameters k_{ij}; thus in principle there would be six parameters to fit for every temperature. However, because reaction runs are made at different temperatures, allowance should be made for variable temperature from one run to the other, from 431 to 490 K. It is thus necessary to introduce the activation energy and the preexponential factor for the kinetic constants.

Table 6. Arrhenius Constants for the Kinetic Coefficients for Sunflower Oil Hydrogenation on Pd/C in SC Propane, $k_{ij} = \exp[A - B/T]$

	A	B (K)	k_{ij} at 444 K	k_{ij} at 490 K
k_{21}*	0.479	4317	1.004×10^{-4}	2.69×10^{-4}
k_{22}*	—	—	2.930×10^{-6}	—
k_{11}**	57.220	31964	0.277×10^{-5}	2.38×10^{-4}
k_{12}**	26.510	17902	0.277×10^{-5}	3.677×10^{-5}
k_o*	1.346	4205	3.469×10^{-4}	7.391×10^{-4}
k_e*	−6.513	—	1.456×10^{-3}	—

See rate expressions on Eqs. 2–6.
*$mol^{-0.5}$ ($m^{4.5}$) kg^{-1} s^{-1}.
**mol^{-1} (m^6) kg^{-1} s^{-1}.

The resulting expression results in a nonlinear problem to fit the reactor outlet concentrations by guessing the 12 (k_0 and E) parameters. The system of equations for the CSTR was solved for the concentrations using the Newton–Raphson method. To estimate the kinetic parameters for the 25 reaction runs a nonlinear least-squares concentrations error minimization algorithm with restrictions was used. The parity plots for the exit concentrations for the optimum values of the kinetic constant are given in Figure 12. In these 25 runs, the accuracy is different depending on the species; for example, hydrogen uptake is very accurately fitted, whereas stearic ester is less well predicted. The *trans*-content is also well predicted with the present kinetic model (see Figure 12). Shown in Table 6 are the Arrhenius expressions for the kinetic constants. It is seen that, because of a slight reduction in iodine values (inlet IV = 130, exit IV = 90), the kinetic constants for stearic ester formation may have more error.

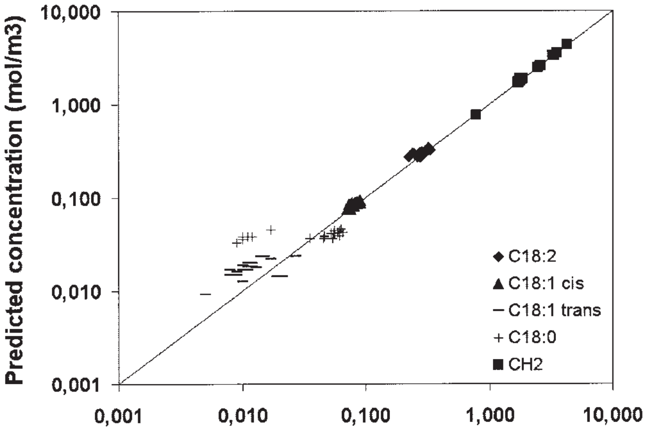

Figure 12. Parity plot of component concentrations in CSTR vs. those predicted by kinetic model. See Eqs. 2–7 with fitted parameters (Table 6).

Conclusions

In this work we report in the fluid-phase hydrogenation on sunflower oil in dense propane with 1 mol % vegetable oil, 9% H_2, and 90% propane. The reaction is run continuously in a single-fluid phase, using a laboratory setup. The catalyst is 2% Pd supported on C.

A wide range of hydrogenation products can be obtained with certain plastic characteristics for further food application by tuning the reaction conditions. The experimental results show that one principal advantage of using propane as a supercritical fluid is the low *trans* acid content, as well as low stearic acid, compared with that of the conventional process.

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Notation

A = parameter in equation for $k = \exp(A - B/T)$
B = activation temperature, $B = E/R_g$, K
C_i = molar concentration of fatty ester i, mol m^{-3}
F_i = molar flow of species i, mol s^{-1}
E = activation energy, J mol^{-1}
K_i = VLE constant. $K_i = y_i/x_i$, where $i = 1$ for SCF and $i = 2$ for sunflower oil
k_{ij} = kinetic rate constant, $mol^{-0.5}(m^{4.5})$ kg^{-1} s^{-1} or $mol^{-1}(m^{6})$ kg^{-1} s^{-1}
LHSV = liquid oil feed (cm^3 h^{-1}) divided by catalyst volume (cm^3), h^{-1}
IV = iodine value (g I_2/100 g oil): 1 IV = 36 mol H_2/m^3 oil
p = probability of making a Type 1 error (that is, rejecting the null hypothesis when it is true)
R_g = gas-law constant, 8.314 J K^{-1} mol^{-1}
r_i = global reaction rate of species i, mol s^{-1} kg^{-1}

W = mass of catalyst, kg
Y = predicted responses in Eq. 1, (IV or wt % *trans*)

Greek letters

β = regression coefficients in Eq. 1
ϵ = error term in Eq. 1

Acronyms

L = linoleic ester, C18:2
LHSV = liquid oil hourly space velocity, h^{-1}
O = oleic triglyceride ester, *cis* C18:1
E = elaidaic triglyceryde ester, *trans* C18:1
S = stearic triglyceryde ester, C18:0

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