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Overcoming Mass-Transfer Limitations in Partial Hydrogenation of Soybean Oil Using Metal-Decorated Polymeric Membranes

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The conventional soybean oil hydrogenation process (metal catalyst on solid support particles slurried in oil, H_2 bubbled through the oil) is compared with metal-decorated integral-asymmetric polyetherimide (PEI) membranes, as far as changes in temperature and pressure are concerned. Using metal-decorated polymeric membranes, H_2 is supplied to the catalytic sites by permeation from the membrane substructure. As opposed to the slurry process, metal-decorated membranes show only slightly increased trans fatty acid (TFA) formation when the temperature is raised (50–90°C) to accelerate the process. This is likely due to the efficient and to some extent self-regulating H_2 supply directly to the catalytic sites on the membrane skin. The hydrogenation rate and TFA formation of the metal-decorated membrane process show a minor dependence on pressure. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 2450–2457, 2011

Keywords: metal-decortaed polymeric membranes, membrane reactor, trans fatty acids, partial hydrogenation

Introduction

Multiphase reactions are widely used in the chemical-, petrochemical-, biotechnology-, and food processing industries. Multiphase reactions are often constrained by mass-transfer limitations, which may lead to low-conversion rates and undesirable product distribution.[1,2]

The partial hydrogenation of vegetable oil is an important multiphase reaction in the food industry, used to improve the oxidative stability and increase the solid fat content in vegetable oil. In the United States alone, the annual production of margarines and shortenings was about 8 billion pounds in 2007.[3] Partial hydrogenation is a three phase (gas-liquid-solid) reaction with hydrogen as a gas, oil as a liquid, and the catalyst as a solid slurried in the oil. Industrial hydrogenation of vegetable oil is carried out in a stirred batch autoclave (Figure 1a, 30,000–90,000 pound oil per batch, reaction time, 100 rpm impeller, equipped with heating/cooling coils[4]) over a nickel based catalyst in a slurry at 110–190°C, 30–70 psi hydrogen pressure, with 0.01–0.15 wt % Ni catalyst[2] generally supported on kieselguhr or silica-alumina particles.[5] This approach relies on the dissolution of hydrogen in the oil followed by transport of dissolved hydrogen initially by convection and finally by diffusion through the stagnant boundary layer of the particles to the catalytic sites.

The vegetable oil hydrogenation process can be described by the Horiuti–Polanyi Mechanism.[6,7] The hydrogen dissolves in liquid oil, diffuses through the stagnant oil layer near the catalyst particles, and is finally adsorbed on the catalyst surface where it dissociates into two adsorbed hydrogen atoms. The hydrogen atoms are thought to react with adsorbed fatty acid molecules to form an unstable half hydrogenated intermediate complex. If the concentration of hydrogen at the catalyst surface is high, the addition of a second H atom to the half hydrogenated intermediate

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dominates over isomerization reactions. When the hydrogen coverage of the surface is low, abstraction of hydrogen may be more likely than insertion,[2] thus, promoting isomerization and formation of the undesirable trans fatty acid (TFA).

In the conventional slurry reactor design, low solubility of hydrogen in oil leads to increased mass-transfer limitations and a scarcity of hydrogen at the catalyst surface. This promotes the isomerization reaction at the expense of hydrogenation and results in significant amounts of TFAs.

Hydrogen mass transfer to the catalytic sites has been recognized as the major limiting step in the conventional hydrogenation process[2] and many modifications of reactor designs[8–10] and processes[11,12] have been evaluated. A more recent type of reactor for three phase reactions is a membrane contactor. In this type of reactor, the gas and liquid reactants are allowed to come in direct contact with each other without the need for the dispersion of one phase into the other. Recently,[13] we demonstrated the hydrogenation of soybean oil using a metal-decorated integral-asymmetric polymeric membrane with a nonporous skin. The metal (platinum)-decorated polymeric membrane produced significantly lower TFAs when compared with the conventional slurry approach (4 wt % total TFA at iodine value (IV) 95 when compared with 10 wt % for slurry reactor[13]). A comparison of the current approach with other novel approaches such as electrochemical reactor, porous membrane reactor, and hydrogenation under supercritical conditions was also studied. Metal-decorated polymeric membranes resulted in similar levels of TFAs as the electrochemical reactor and supercritical hydrogenation, but at conditions compatible with the existing equipment in hydrogenation facilities. The process investigated here appears somewhat simpler than operating the electrochemical reactor. The type of polymer membranes needed is routinely produced on the industrial scale, and the sputtering process to apply the metal to polymers is well known from the industrial manufacture of metal-coated fibers and films.

Figure 1b schematically shows a metal-decorated polymeric membrane. An integral-asymmetric polymeric membrane with high-gas flux and selectivity for hydrogen and negligible permeability to vegetable oil is the base material. The polymeric membrane consists of a highly porous substructure with a thin (~0.1–0.3 μm), dense, and essentially defect-free layer known as the membrane skin. Subsequently, the membrane skin is decorated with palladium or platinum catalyst using magnetron sputtering. The metal was deposited as a network of large interconnected islands with some exposed polymer membrane area. One of our previous studies showed that the catalyst distribution as obtained gave high-hydrogenation rates with minimum formation of TFA.[14]

Temperature and pressure are important parameters in reactor design. Operation at higher temperatures is often desired due to increased reaction rates. However, for the case of hydrogenation of vegetable oil in a traditional slurry reactor, an increase in temperature increases the rate of formation of TFA due to (1) decreased hydrogen solubility in oil and (2) an increased hydrogenation rate leading to hydrogen starvation of the catalyst. Increased hydrogen pressures can be used to increase the solubility of hydrogen in oil and reduce the formation of TFAs.[6] Economical and operational issues arise if the hydrogen pressure is increased significantly. The metal-decorated membrane allows low TFA formation at pressures and temperatures compatible with existing facilities.[13]

If metal-decorated polymeric membranes are able to maintain a high concentration of hydrogen at the catalyst surface even at increased temperatures, one could obtain increased reaction rates without the increase in TFA normally observed through hydrogen starvation in the conventional slurry process. Furthermore, because the membrane reactor supplies hydrogen directly to the catalyst, modest system pressures should still be sufficient if high performance polymeric membranes with thin dense skins are used.

This work studies the impact of pressure and temperature on partial hydrogenation of vegetable oil using platinum- and palladium-decorated polymeric membranes. The behavior in regard to pressure and temperature is compared with that of the conventional slurry approach under similar conditions.

Experimental

Materials

Soybean oil (IV = 129–131) was obtained from MP Biomedicals (Solon, OH). The composition of soybean oil as measured in our laboratory is (in weight percent): C16:0, 11.6–12.0; C18:0, 4.3–4.4; C18:1, 21.6–23.8; C18:2, 51.6–53.3; C18:3, 7.1–7.8; total TFAs, 0.7–1.2; C18:1 trans, 0.0; C14:0–C24:0, 0.9–1.5. Acetic acid (HPLC grade), acetone (99.5%), *p*-xylene (99.9%), and dicholoromethane (99.9%) used in membrane casting were obtained from Fisher Scientific (Rochester, NY). 1,1,2,2-tetrachloroethane (98%) was obtained from Sigma Aldrich (St. Louis, MO). Polyetherimide (PEI) to cast asymmetric membranes was obtained from General Electric (Ultem-1000, Huntersville, NC). Platinum (99.95 wt % platinum) and palladium (99.95 wt % palladium) targets for sputtering were obtained from Ted Pella (Redding, CA).

Membrane preparation and characterization

Integral-Asymmetric Membranes. The integral-asymmetric PEI membranes used in this study were fabricated in our laboratory using the phase inversion process as described by Peinemann.[15] Circular stamps (4.6 cm diameter) were cut from the hand-cast membrane sheets and tested for their gas flux using a constant-volume variable-pressure apparatus similar to the one described elsewhere[16] at 25°C and 50 psig feed pressure. The pressure and area normalized gas flux J in gas permeation units [GPU; 10^{-6} cm^3(STP)/(cm^2 cmHg s)] and the ideal gas selectivity ($\alpha_{H_2/N_2} = J_{H_2}/J_{N_2}$) are calculated to judge the quality of the membrane skin. The hydrogen flux of these membranes can be as high as 100 GPU with α_{H_2/N_2} up to 181 at 25°C. This approaches the α_{H_2/N_2} for thick PEI films.[17,18] Any defects in the membrane skin result in α_{H_2/N_2} lower than the thick film value (sometimes termed intrinsic selectivity) of 181. The α_{H_2/N_2} of integral-asymmetric membranes can even exceed the "intrinsic" value for thick films of the same polymer due to accelerated aging of the very thin selective skin layer compared with thick films.[19–21]

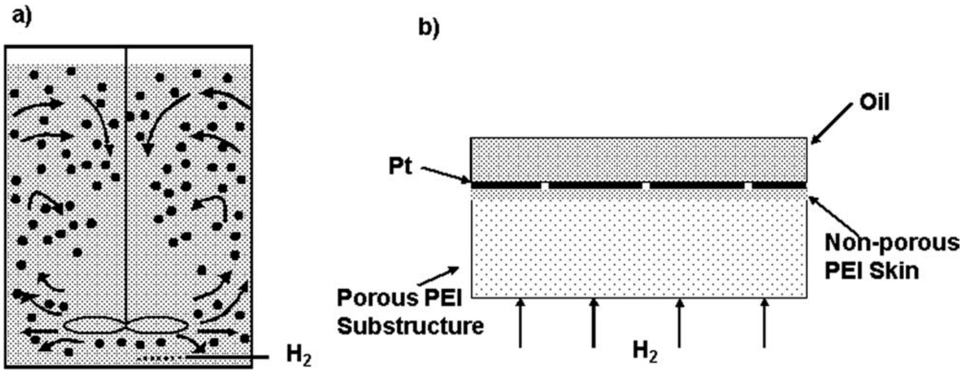

Figure 1. Schematic of the conventional batch slurry reactor and the metal-decorated asymmetric polymer membrane reactor for partial hydrogenation of soybean oil.

Metal-Decorated Integral-Asymmetric Membranes by Sputtering. The membranes were sputtered on the skin side with palladium or platinum metal using a DESK II magnetron sputter (Denton Vacuum, Moorestown, NJ; for 9 sec at 45 mA, 100 mtorr) and were retested for their gas transport properties after sputtering. These sputtered membranes are here also referred to as metal-decorated. The gas flux of the membranes is generally reduced after sputtering as can be expected due to coverage of some high-permeability polymer membrane area with a low-permeability metal layer. Gas selectivities after sputtering also change depending among other factors such as the initial α_{H_2/N_2} (representing the quality of the asymmetric polymer membrane), the extent of coverage of the membrane surface with metal, and the possible modification of the membrane polymer skin layer itself by the sputtering plasma.[22,23]

The morphology of the membrane surface and the catalyst distribution after sputter deposition was studied using transmission electron microscopy (TEM). For this purpose, a thin layer (<100 nm) of PEI was spin coated on a TEM grid (2000 mesh copper grid, Electron Microscopy Sciences, Hatfield, PA) followed by Pd or Pt sputtering under the same conditions (25°C, 100 mTorr air, 45 mA, 9 sec) as used to produce membrane for the hydrogenation runs. Figure 2 shows the TEM of PEI films after sputtering with platinum and palladium. At this loading both platinum and palladium appear in the form of an interconnected network of islands with interstitial exposed PEI areas.

Hydrogenation setup and procedures

The metal-sputtered membrane was installed in a stainless steel 47-mm filter holder (model XX4404700, Millipore, Billerica, MA), and the metal catalyst was then reduced by purging H$_2$ over the skin side (60°C, 15 hr). Soybean oil was then circulated from a nitrogen-blanketed reservoir vessel over the skin side (metal-decorated) of the membrane using a gear pump (Series GA, Micropump, Vancouver, WA; 25 g oil/min) with temperature and pressure monitoring and control. Details of the experimental setup are provided elsewhere.[13] UHP hydrogen was supplied from the porous substructure side of the membrane at the required pressure after the desired reaction temperature was attained. The oil side pressure was always maintained at 10 psi above the H$_2$ pressure by blanketing the oil reservoir with N$_2$ to prevent mechanical damage

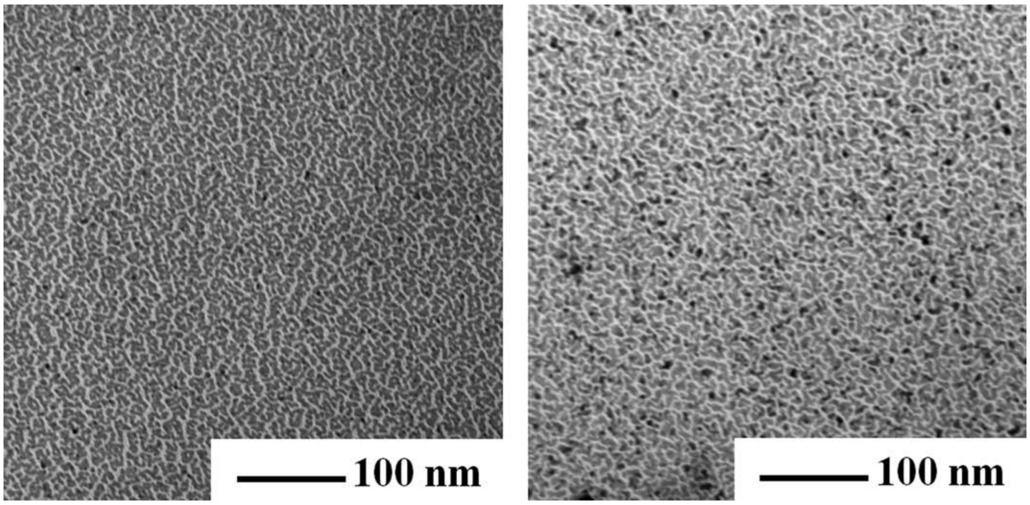

Figure 2. TEMs of the surface of PEI films sputtered with palladium (left image), platinum (right image) for 9 s.

The images show an interconnected network of Pd/Pt islands formed at the surface of the PEI film.

Table 1. Properties of Membranes and Hydrogenation Conditions Used in the Study

H_2 Flux (GPU)	Ideal Gas Selectivity α_{H_2/N_2}	Temperature	Pressure (psig)
Catalyst: Palladium, 1.4 $\mu g\ cm^{-2}$			
12	164	50	50
81	6	70	50
59	145	90	50
7	100	70	50-200
Catalyst: Platinum, 3.4 $\mu g\ cm^{-2}$			
4	18	60	50
10	5	70	50
46	64	90	50
7	14	70	50-200

(blowout) because the skin side of the membrane was not supported.

Analysis

Oil samples were converted to fatty acid methyl esters (FAMEs) following American Oil Chemists Society (AOCS) official method Ce 2-66 (alternate[24]). FAMEs were analyzed by gas chromatography (GC; 100m CP-Sil 88 column, Hewlett-Packard 6890 series gas chromatograph). AOCS official method Ce 1h-05 was followed for the analysis of fatty acids (Injection port and column 250 and 181°C, respectively, He carrier gas 1 mL/min, split ratio 1:100). The extent of hydrogenation is represented by its IV, which is the mass of iodine in grams that is consumed under standard conditions by 100 g of a lipid.[2] The IV of hydrogenated oil was calculated from the composition obtained by GC analysis using Eq. 1.[25]

$$\mathrm{IV} = (\%\mathrm{C16{:}1} \times 0.9502) + (\%\mathrm{C18{:}1} \times 0.8598) + (\%\mathrm{C18{:}2} \times 1.7315) + (\%\mathrm{C18{:}3} \times 2.6152) \quad (1)$$

Hydrogenation selectivity S

Hydrogenation of natural oil such as soybean oil is quite complex due to the number of components present in the oil. Selectivities are calculated here by assuming first-order reactions as presented in Eq. 2.[2] The hydrogenation selectivities can then be calculated using the experimental composition data from our experiments.[26]

$$C18{:}3(Ln) \xrightarrow{k_1} C18{:}2(L) \xrightarrow{k_2} C18{:}1\,(O) \xrightarrow{k_3} C18{:}0(S) \quad (2)$$

where k_1, k_2, and k_3 are pseudo-first-order rate constants. The linolenate (S_{Ln}), Linoleate (S_{L}), and isomerization (S_{i}) selectivities are defined as

$$S_{\mathrm{Ln}} = \frac{k_1}{k_2} \quad (3)$$

$$S_{\mathrm{L}} = \frac{k_2}{k_3} \quad (4)$$

$$S_{\mathrm{i}} = \frac{\Delta \mathrm{trans}}{\Delta \mathrm{IV}} \quad (5)$$

The simplified definition of hydrogenation selectivities assumes the absence of positional selectivity, equal rates of fatty acid isomers, absence of any shunt reactions, and identical dependence of different fatty acids on hydrogen concentration. This simplified approach of calculating hydrogenation selectivities is widely accepted by fat chemists.[2]

Results and Discussion

Partial hydrogenation of soybean oil was performed at 50–90°C and 50–200 psig H_2 pressure using Pd- and Pt-sputtered integral-asymmetric polymer membranes (see Table 1 for membrane properties and experimental conditions). It should be noted that the H_2 pressure is applied to the porous substructure of the asymmetric metal-decorated membranes. The hydrostatic pressure on the skin (oil-) side of the membrane always exceeds the H_2 pressure to prevent membrane blowout. This was done with a nitrogen blanket on the oil circulation reservoir.

The hand-cast membranes studied here have a range of hydrogen fluxes J_{H_2} and selectivities α_{H_2/N_2} depending on the skin thickness and the presence/absence of skin defects that may allow some gas permeation by convection rather than diffusion through the skin. A brief discussion of the effect of membrane properties on the hydrogenation rate and TFA formation is provided below.

An earlier study in our laboratory evaluated platinum-decorated polymeric membranes having a range of hydrogen fluxes, skin defects, and catalyst loadings.[14] It was observed that hydrogenation rates initially increase with the H_2 flux of the metal-decorated membranes but then level off, indicating that an abundance of H_2 is available and the process becomes limited by available catalyst sites. The H_2 flux and α_{H_2/N_2} showed little influence on TFA formation.

Based on our earlier work,[14] membranes were chosen that were known to supply sufficient H_2 at the given temperature so that the supply of hydrogen is not limiting.

Effect of temperature

It is desirable to operate at high temperatures due to higher reaction rates; however, higher temperatures conventionally also lead to increased formation of TFAs in slurry reactors because the hydrogen solubility decreases with

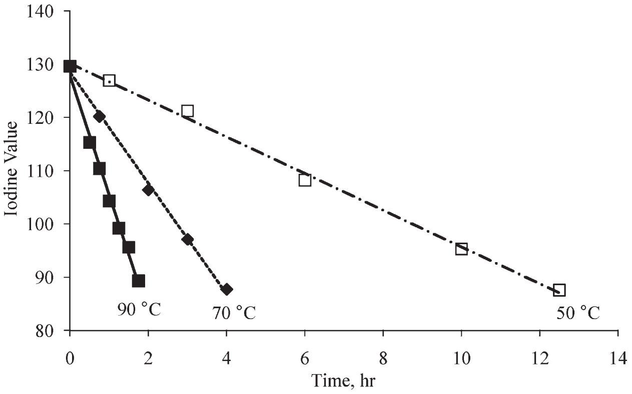

Figure 3. Increasing temperature accelerates the partial hydrogenation of soybean oil over a palladium-decorated integral-asymmetric polymer membrane.

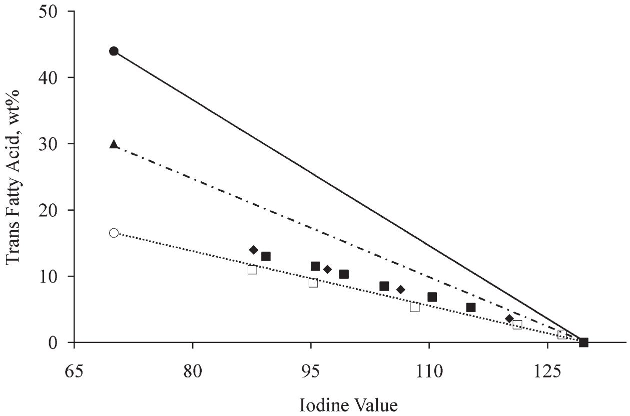

Figure 4. The increase in trans fatty acid formation with temperature during partial hydrogenation of soybean oil using the conventional slurry approach (Pd on alumina slurry[24] 50°C (○), 70°C (▲), 90°C (●), lines are drawn to aid the eye and do not suggest a linear relationship) is essentially reduced with the Pd-decorated asymmetric polymer membrane even at 90°C [Pd-sputtered asymmetric polymer membrane 50°C (□), 70°C (◆), 90°C (■)].

This supports the notion of the high H_2 availability at the catalytic sites for the membrane-based system can be effectively maintained at a variety of conditions.

increasing temperature. This section compares the influence of temperature on hydrogenation rate, cis-trans isomerization, and hydrogenation selectivities for membrane-based and slurry-based catalysis under similar conditions.

Hydrogenation Rate. Figure 3 shows the strong increase of the hydrogenation rate (represented by the IV) with temperature using a Pd-decorated polymeric membrane at 50 psig H_2 pressure. The hydrogenation rate was 3.4 IV hr^{-1} at 50°C, increased to 10.4 IV hr^{-1} at 70°C, and to 22.4 IV hr^{-1} at 90°C. The hydrogenation rate for a Pt-decorated polymeric membrane was not significant at 50°C but increased to 3.6 IV hr^{-1} at 60°C and 17.2 IV hr^{-1} at 90°C. The hydrogenation rate constant for the palladium-decorated polymeric membrane at 50, 70, and 90°C was 0.39, 1.25, and 2.73 (kg of oil g of $metal^{-1}$ min^{-1}). Although in the slurry reactor system using palladium as catalyst, it was 0.22 (kg of oil g of $metal^{-1}$ min^{-1}) at 90°C and 50 psig.[27,28] The higher rate constant in the Pd-decorated polymeric membrane reactor system indicates more effective use of the available catalyst when compared with the slurry reactor systems where mass-transfer limitations and hydrogen scarcity at catalyst surface lead to lower reaction rates.

The apparent activation energy (E_a) for hydrogenation for Pd as catalyst was 11.2 kcal mol^{-1} and that for Pt was 11.7 kcal mol^{-1}. The slightly higher activation energy for platinum is due to the lower activity of Pt when compared with Pd[2]. Hsu et al.[28] observed an E_a of 7.7 kcal mol^{-1} for Pd catalyst in a slurry reactor. Under conditions, which measure only the catalytic properties, the measured activation energy should be independent of the type of reactor. Lower apparent activation energies are obtained in conditions where the availability of one reactant is limited. Such mass-transfer limitations appear to be present in the slurry reactor system reported by Hsu.[28]

TFA Formation. In a three-phase slurry reactor, an increase in temperature increases the rate of H_2 consumption, concurrent with a decrease in the supply rate of H_2 due to decreased solubility of H_2 in oil. Therefore, a temperature increase for the slurry reactor increases the H_2 starvation of the catalyst and leads to increased TFA formation. In the metal-decorated polymeric membrane case, H_2 is supplied to the catalyst "on demand" with the maximum rate of supply at a given H_2 pressure limited by the membrane characteristics. Additionally, the permeability of H_2 through the membrane polymer PEI increases with temperature with an E_a of about 3.2 kcal mol^{-1}.[18] If membranes with few or no skin defects and sufficient H_2 flux are used, an increase in temperature should lead to increased availability of H_2 at catalytic sites and, thus, reduce TFA.

Figure 4 supports the above argument and shows that a temperature increase does not significantly change the TFA formation for the metal-decorated membrane, whereas the slurry system (Pd on carbon) shows a clear increase of TFA with temperature.[27]

A similar trend confirming the mechanism described above is seen for Pt-decorated polymeric membranes (Figure 5). The amount of TFA formed at an IV of 90 increases only slightly from 2.2 wt % at 60°C to 3.6 wt % at 90°C. However, the Pt/C slurry reactor produced about 8.4 wt % TFA at 70°C and an IV of 94. In summary, hydrogenation tests with metal-decorated asymmetric membranes show the opportunity to maximize hydrogenation rates through temperature increase nearly without the detrimental increase in TFA's seen for the traditional slurry system when temperature is increased.

Hydrogenation Selectivity. The hydrogenation selectivity *S* describes the preference of hydrogenation of polyenes over

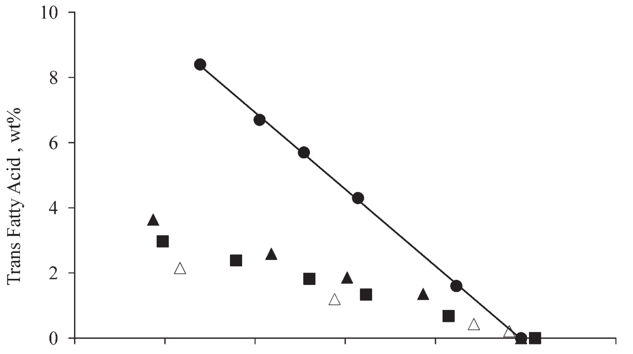

Figure 5. The C18:1 trans fatty acid content increase during partial hydrogenation of soybean oil using the metal-decorated polymer membranes [Pt-sputtered asymmetric polymer membrane, 60°C (Δ), 70°C (■), 90°C (▲)] is much lower than for the slurry reactor[13], [Pt on carbon slurry, 70°C (●)].

Higher temperatures with increased hydrogenation rates can be used with the membrane approach while still maintaining low trans fat formation.

Table 2. Effect of Temperature and Pressure on Hydrogenation Selectivities for Pd- and Pt-Decorated Polymeric Membranes

Temperature (°C)	H_2 Pressure (psig)	Linolenic Selectivity (S_{Ln})	Linoleic Selectivity (S_L)	Specific Isomerization Index (S_i)
Catalyst: Palladium				
50	50	1.7	4.2	0.28
70	50	1.7	3.0	0.33
90	50	1.2	1.6	0.32
70	200	1.2	3.2	0.28
Catalyst: Platinum				
60	50	1.6	1.0	0.05
70	50	1.4	1.1	0.06
90	50	1.3	0.9	0.09
70	200	1.4	1.1	0.04

Table 3. Activation Energy

E_{a1} (kcal mol^{-1})	E_{a2} (kcal mol^{-1})	E_{a3} (kcal mol^{-1})
Catalyst: Palladium		
7.8 ($R^2 = 0.896$)	10.0 ($R^2 = 0.985$)	15.6 ($R^2 = 1.000$)
Catalyst: Platinum		
10.5 ($R^2 = 0.985$)	12.3 ($R^2 = 0.972$)	13.5 ($R^2 = 0.997$)

monoenes. The desirable case is if *S* is very high so that virtually no saturated compounds are formed until almost all polyene has been hydrogenated.[29] *S* is sensitive to the conditions at the catalyst surface.[30] If the availability of adsorbed hydrogen on the catalyst surface is low, polyenes are preferentially adsorbed and multibonded on the catalyst surface displacing less strongly bonded monoenes.[31] Thus, polyenes are preferentially hydrogenated. However, when the degree of adsorbed hydrogen on the catalyst surface is high, a significant portion of polyenes may never reach the polybonded state and, thus, will have an initial more weakly bonded state similar to monoenes. This promotes hydrogenation of both polyenes and monoenes,[31] thus, decreasing hydrogenation selectivity.

For conventional slurry systems, an increase in temperature leads to a decrease in surface coverage of adsorbed hydrogen and ultimately increases the hydrogenation selectivity. The trend for metal-decorated polymeric membranes is opposite to what is observed in slurry systems (Table 2). The linoleic selectivity decreased almost 60% with an increase in temperature from 50 to 90°C. The linolenic and linoleic selectivity at 90°C and 50 psig were 1.2 and 1.6, respectively, when compared with 1.7 and 6.1 for the slurry reactor under similar conditions.[28] The lower linoleic selectivity and its decrease with the increase in temperature for palladium-decorated polymeric membranes can be attributed to increased hydrogen coverage of the catalyst surface at higher temperature because of the high flux membranes used (59 GPU at 90°C when compared with 12 GPU at 50°C). This is also illustrated by Figure 6 where at an IV of 90, hydrogenation at 90°C resulted in 25% more saturates and 20 percent less monoenes, when compared with 50°C. Higher C18:3 at 90°C than at 50°C may also be attributed to increased availability of hydrogen at 90°C due to the high flux membrane used at 90°C. The conditions at 50°C (lower hydrogen availability) promoted the preferential hydrogenation of polyenes, whereas the conditions at 90°C promoted hydrogenation of both polyenes and monoenes, thereby resulting in higher C18:3 at 90°C for a given IV.

The apparent activation energies for the individual rate constants were calculated from the plot of rate constants as obtained from Eq. 2 (Table 3). Both for palladium- and platinum-decorated membranes, the order of activation energy was, $E_{a3} > E_{a2} > E_{a1}$. However, for slurry reactor systems the activation energy for linoleate rate constants is higher than that of oleate rate constants.[2] The different trends observed here can be attributed to the higher hydrogen concentration at higher temperatures for the case of metal-decorated polymeric membranes. This is opposed to the case for slurry reactors, which experience a decrease in hydrogen

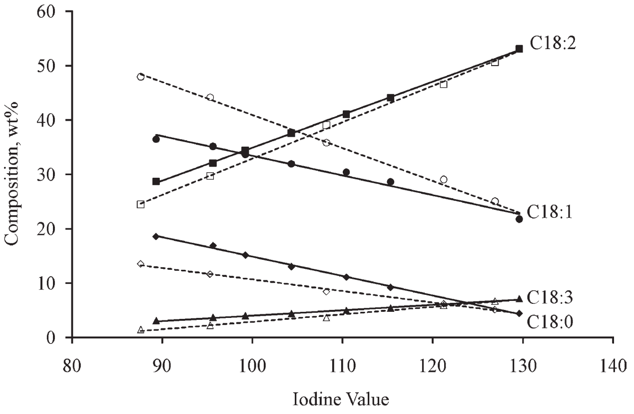

Figure 6. Composition profiles for hydrogenation of soybean oil using Pd-decorated asymmetric polymer membranes at 50°C (-------) and 90°C (______).

Hydrogenation at higher temperatures resulted in higher saturates and lower monoenes due to possible higher concentration of hydrogen at catalyst surface at higher temperatures.

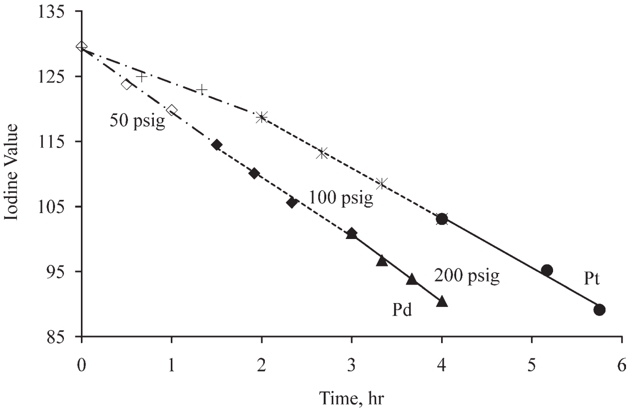

Figure 7. Effect of pressure on hydrogenation rate for Pd- and Pt-decorated polymeric membranes, 70°C.

Pd membrane at 50 psig (◇), 100 psig (◆), and 200 psig (▲); Pt membrane at 50 psig (+), 100 psig (x), and 200 psig (●). Both Pd- and Pt-decorated polymeric membrane reactors show a modest dependence of hydrogenation rate on pressure.

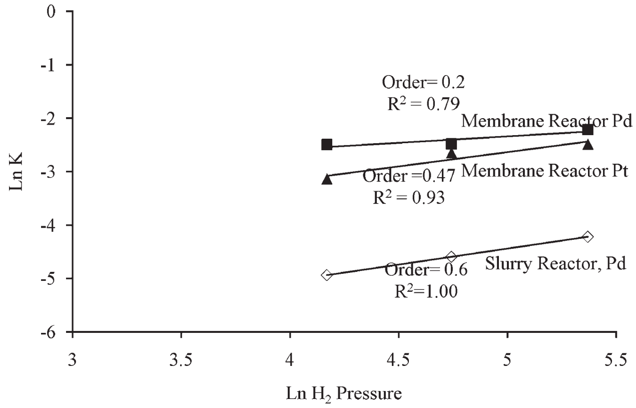

Figure 8. Effect of pressure on the hydrogenation rate of a Pd-sputtered and a Pt-decorated asymmetric polymer membrane, and Pd/alumina slurry reactor,[23] all at 70°C.

The lower order for Pd-decorated polymer membrane reactor indicates the insensitivity of hydrogenation to pressure.

availability at the catalyst surface as temperature is increased.

Effect of pressure

In conventional slurry reactors, the rate of hydrogenation depends on the concentration of hydrogen in the bulk oil,[7] which controls the catalyst's surface coverage of hydrogen. An increase in hydrogen pressure increases the solubility of H_2 in oil, thus, increasing the hydrogenation rate and decreasing TFA formation. For hydrogenation of soybean oil using Pd-Al_2O_3 catalyst, Hsu et al. observed a reaction order of 0.6, with respect to H_2.[28] Other authors have observed reaction orders in the range of 0.2–1.6, for palladium slurry reactors.[32,33] The pressure dependencies substantially lower than unity[32] have been attributed to the presence of intraparticle H_2 diffusion limitations.[2] Boyes et al.[33] reported a reaction order higher than unity with Pd/C catalyst, which was attributed to simultaneous reaction involving more than one hydrogen molecule.

For the case of metal-decorated polymeric membranes, an increase in hydrogen pressure increases the hydrogen flux of the membrane linearly according to the following equation:

$$J_{H_2} = P_{H_2}\frac{\Delta p}{l} \tag{9}$$

where J_{H_2} is the hydrogen flux through the membrane in cm^3 (STP) cm^{-2} s^{-1}, P_{H_2} is the permeability coefficient, usually expressed in terms of Barrer, 1 Barrer $=10^{-10}$ cc(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$, Δp is the H_2 partial pressure difference across the membrane in cmHg, and l is the effective skin thickness of the membrane in cm. For a given membrane during a hydrogenation run, the H_2 flux depends not only on the hydrostatic H_2 pressure applied to the gas side of the membrane but also on the rate of hydrogen consumption, which governs the partial pressure of H_2 in the stagnant oil layer near the catalyst. If dissolved H_2 builds up on the oil side then the driving force for H_2 permeation will diminish, which represents a type of self-limiting mechanism.

To study the effect of H_2 pressure on hydrogenation using a Pd-decorated polymeric membrane, a hydrogenation run was started at 50 psig H_2 and 70°C, the pressure was increased to 100 psig at IV 115, and then increased to 200 psig at IV 100, ending at IV 90. This results in an initial hydrogen partial pressure difference of 50 psig across the membrane (ignoring any hydrogen accumulation by slow reaction), 100 psig at IV 115–110, and 200 psig at IV 100–90. The palladium membrane used for the hydrogenation run had a hydrogen flux of 7 GPU and α_{H_2/N_2} of 100. A similar procedure was followed using a Pt-decorated polymeric membrane (7 GPU H_2, $\alpha_{H_2/N_2} = 14$). These H_2 fluxes were relatively low compared with the bulk of the membranes that were manufactured.

Hydrogenation Rate. For the Pd-decorated polymeric membrane, an increase in H_2 pressure from 50 psig to 200 psig resulted in a minor increase in hydrogenation rate (Figure 7, 9.3 IV hr^{-1}, 50 psig; 10.6 IV hr^{-1}, 200 psig). The order of reaction with respect to H_2 pressure was 0.2 (Figure 8). The modest dependence of the rate on H_2 pressure may be attributable to the insensitivity of hydrogen availability at the catalytic sites to system pressure because of the already high concentration of hydrogen on the catalyst surface. Clearly, any increase in H_2 pressure will, thus, not have as large an effect as observed in conventional slurry reactors.

The Pt-decorated polymeric membrane showed a slightly greater dependence of hydrogenation rate on hydrogen pressure. The order of reaction with respect to hydrogen pressure was 0.5. The Pt-decorated membrane had about the same J_{H_2} as the Pd-decorated membrane but a much lower α_{H_2/N_2} indicating the presence of more defects in the skin of the Pt-decorated membrane. This may result in lower overall surface coverage of the catalyst by hydrogen for the Pt membrane because more hydrogen will be primarily supplied from mass transport through isolated defects in the membrane skin as "point sources" versus the evenly distributed transport by solution/diffusion through the skin. This, in turn, can then reduce the hydrogenation rate somewhat, reflected in a reduced slope of the IV versus time trace for the Pd versus the Pt-decorated membrane.

Isomerization and Hydrogenation Selectivity. For Pd-decorated membranes, the isomerization index decreased slightly from 0.35 to 0.28 with an increase in H_2 pressure from 50 to 100 psig. There was no change in isomerization index from 100 to 200 psig H_2. For the case of the Pt-decorated membranes, the isomerization index remained in the range of 0.04–0.07 from 50 to 200 psig H_2 (Table 2). The Linoleic acid selectivities showed no change for both Pd- and Pt-decorated membranes with an increase in pressure from 50 to 200 psig.

An increase in the H_2 pressure did not significantly impact the isomerization indices because hydrogen probably was already abundant at the catalytic sites even at the lowest pressure.

Conclusions

Metal-decorated integral-asymmetric polyimide membranes were used to partially hydrogenate soybean oil with minimized TFA formation in comparison with the conventional three-phase slurry process. H_2 is supplied by diffusion from the porous support side of the membrane emerging as dissolved gas at or near the catalytic sites on the membrane skin exposed to the oil. A temperature increase was beneficial for the Pd- and Pt-decorated polymeric membranes because the hydrogenation rate increased, whereas TFA formation remained low. This is in contrast to the conventional slurry process where mass-transfer limitations lead to increasing TFA formation when the temperature is raised. Increasing the H_2 pressure did not significantly impact the membrane-based process.

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Notation

α_{H_2/N_2} = ideal gas selectivity (ratio of normalized single gas flux of hydrogen and nitrogen)
E_{a1} = apparent activation energy for hydrogenation of linolenic acid to linoleic acid, kcal mol^{-1}
E_{a2} = apparent activation energy for hydrogenation of linoleic acid to oleic acid, kcal mol^{-1}
E_{a3} = apparent activation energy for hydrogenation of oleic acid to stearic acid, kcal mol^{-1}
J_{H_2} = hydrogen flux through the membrane, cm^3 (STP) cm^{-2} s^{-1}
J_{N_2} = nitrogen flux through the membrane, cm^3 (STP) cm^{-2} s^{-1}
k_1 = pseudo-first-order rate constant for hydrogenation of linolenic acid to linoleic acid, (kg of oil g of $metal^{-1}$ min^{-1})
k_2 = pseudo-first-order rate constant for hydrogenation of linoleic acid to oleic acid, (kg of oil g of $metal^{-1}$ min^{-1})
k_3 = pseudo-first-order rate constant for hydrogenation of oleic acid to stearic acid, (kg of oil g of $metal^{-1}$ min^{-1})
l = effective skin thickness of the membrane, cm
ΔP = hydrogen partial pressure difference across the membrane, cmHg
P_{H_2} = permeability coefficient of hydrogen, 10^{-10} cc(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$
S_{Ln} = linolenate hydrogenation selectivity
S_L = linoleate hydrogenation selectivity
S_i = isomerization selectivity

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