

1 **Overcoming mass-transfer limitations in partial hydrogenation of**
2 **soybean oil using metal decorated polymeric membranes**

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7 **Abstract**

8 The conventional soybean oil hydrogenation process (metal catalyst on solid
9 support particles slurried in oil, H₂ bubbled through the oil) is compared to metal-
10 decorated integral-asymmetric polyetherimide (PEI) membranes, as far as changes in
11 temperature and pressure are concerned. Using metal decorated-polymeric membranes,
12 H₂ is supplied to the catalytic sites by permeation from the membrane substructure. As
13 opposed to the slurry process, metal-decorated membranes show only slightly increased
14 trans fatty acid (TFA) formation when the temperature is raised (50-90°C) to accelerate
15 the process. This is likely due to the efficient and to some extent self-regulating H₂
16 supply directly to the catalytic sites on the membrane skin. The hydrogenation rate and
17 TFA formation of the metal decorated membrane process show a minor dependence on
18 pressure.

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21 **Introduction**

22 Multiphase reactions are widely used in the chemical-, petrochemical-,
23 biotechnology-, and food processing industries. Multiphase reactions are often
24 constrained by mass transfer limitations which may lead to low conversion rates and
25 undesirable product distribution.^{1,2}

26 The partial hydrogenation of vegetable oil is an important multiphase reaction in
27 the food industry, used to improve the oxidative stability and increase the solid fat
28 content in vegetable oil. In the U.S. alone, the annual production of margarines and
29 shortenings was about 8 billion pounds in 2007³. Partial hydrogenation is a three phase
30 (gas-liquid-solid) reaction with hydrogen as a gas, oil as a liquid and the catalyst as a
31 solid slurried in the oil. Industrial hydrogenation of vegetable oil is carried out in a
32 stirred batch autoclave (Figure 1a, 30,000-90,000 pound oil per batch, reaction time, 100
33 rpm impeller, equipped with heating/cooling coils⁴) over a nickel based catalyst in a
34 slurry at 110-190°C, 30-70 psi hydrogen pressure, with 0.01-0.15wt% Ni catalyst²
35 generally supported on kieselguhr or silica-alumina particles⁵. This approach relies on
36 the dissolution of hydrogen in the oil followed by transport of dissolved hydrogen
37 initially by convection and finally by diffusion through the stagnant boundary layer of the
38 particles to the catalytic sites.

39 The vegetable oil hydrogenation process can be described by the Horiuti-Polanyi
40 Mechanism^{6, 7}. The hydrogen dissolves in liquid oil, diffuses through the stagnant oil
41 layer near the catalyst particles and is finally adsorbed on the catalyst surface where it
42 dissociates into two adsorbed hydrogen atoms. The hydrogen atoms are thought to react

43 with adsorbed fatty acid molecules to form an unstable half hydrogenated intermediate
44 complex. If the concentration of hydrogen at the catalyst surface is high, the addition of a
45 second H atom to the half hydrogenated intermediate dominates over isomerization
46 reactions. When the hydrogen coverage of the surface is low, abstraction of hydrogen
47 may be more likely than insertion², thus promoting isomerization and formation of the
48 undesirable TFA.

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

53 Hydrogen mass transfer to the catalytic sites has been recognized as the major
54 limiting step in the conventional hydrogenation process² and many modifications of
55 reactor designs⁸⁻¹⁰ and processes^{11, 12} have been evaluated. A more recent type of reactor
56 for three phase reactions is a membrane contactor. In this type of reactor the gas and
57 liquid reactants are allowed to come in direct contact with each other without the need for
58 the dispersion of one phase into the other. Recently¹³, we demonstrated the
59 hydrogenation of soybean oil using a metal decorated integral-asymmetric polymeric
60 membrane with a non-porous skin. The metal (platinum) decorated polymeric membrane
61 produced significantly lower TFAs as compared to the conventional slurry approach (4
62 wt% total TFA at iodine value IV 95 as compared to 10 wt% for slurry reactor¹³). A
63 comparison of the current approach with other novel approaches like electrochemical
64 reactor, porous membrane reactor, and hydrogenation under supercritical conditions was
65 also studied. Metal decorated polymeric membranes resulted in similar levels of TFAs as

66 the electrochemical reactor and supercritical hydrogenation, but at conditions compatible
67 with the existing equipment in hydrogenation facilities. The process investigated here
68 appears somewhat simpler than operating the electrochemical reactor. The type of
69 polymer membranes needed is routinely produced on the industrial scale, and the
70 sputtering process to apply the metal to polymers is well known from the industrial
71 manufacture of metal coated fibers and films.

72 Figure 1b schematically shows a metal decorated polymeric membrane. An
73 integral asymmetric polymeric membrane with high gas flux and selectivity for hydrogen
74 and negligible permeability to vegetable oil is the base material. The polymeric
75 membrane consists of a highly porous substructure with a thin (approximately 0.1-
76 0.3 μm), dense and essentially defect-free layer known as the membrane skin.
77 Subsequently the membrane skin is decorated with palladium or platinum catalyst using
78 magnetron sputtering. The metal was deposited as a network of large interconnected
79 islands with some exposed polymer membrane area. One of our previous studies showed
80 that the catalyst distribution as obtained gave high hydrogenation rates with minimum
81 formation of TFA¹⁴.

82 Temperature and pressure are important parameters in reactor design. Operation
83 at higher temperatures is often desired due to increased reaction rates. However, for the
84 case of hydrogenation of vegetable oil in a traditional slurry reactor, an increase in
85 temperature increases the rate of formation of TFA due to (1) decreased hydrogen
86 solubility in oil and (2) an increased hydrogenation rate leading to hydrogen starvation of
87 the catalyst. Increased hydrogen pressures can be used to increase the solubility of
88 hydrogen in oil and reduce the formation of TFAs⁶. Economical and operational issues

89 arise if the hydrogen pressure is increased significantly. The metal decorated membrane
90 allows low TFA formation at pressures and temperatures compatible with existing
91 facilities¹³.

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

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

103 **Experimental**

104 **Materials**

105 Soybean oil (Iodine Value IV = 129-131) was obtained from MP Biomedicals
106 (Solon, OH). The composition of soybean oil as measured in our laboratory is (in weight
107 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,
108 7.1-7.8; total trans fatty acids, 0.7-1.2; C18:1 trans, 0.0; C14:0-C24:0, 0.9-1.5. Acetic
109 acid (HPLC grade), acetone (99.5%), p-xylene (99.9%), and dichloromethane (99.9%),
110 used in membrane casting were obtained from Fisher Scientific (Rochester, NY). 1,1,2,2-

111 tetrachloroethane (98%) was obtained from Sigma Aldrich (St. Louis, MO). PEI to cast
112 asymmetric membranes was obtained from General Electric (Huntersville, NC, Ultem-
113 1000). Platinum (99.95wt% platinum) and palladium (99.95 wt% palladium) targets for
114 sputtering were obtained from Ted Pella Inc. (Redding, CA).

115 **Membrane preparation and characterization**

116 *Integral-asymmetric membranes*

117 The integral asymmetric PEI membranes used in this study were fabricated in our
118 lab using the phase inversion process as described by Peinemann¹⁵. Circular stamps (4.6
119 cm diameter) were cut from the hand-cast membrane sheets and tested for their gas flux
120 using a constant-volume variable-pressure apparatus similar to the one described
121 elsewhere¹⁶ at 25°C and 50 psig feed pressure. The pressure and area normalized gas
122 flux J in Gas Permeation Units (GPU, 10^{-6} cm³(STP)/ (cm² cmHg s)) and the ideal gas
123 selectivity ($\alpha_{H_2/N_2} = J_{H_2}/J_{N_2}$) are calculated to judge the quality of the membrane skin. The
124 hydrogen flux of these membranes can be as high as 100 GPU with α_{H_2/N_2} up to 181 at
125 25°C. This approaches the α_{H_2/N_2} for thick PEI films^{17, 18}. Any defects in the membrane
126 skin result in α_{H_2/N_2} lower than the thick film value (sometimes termed intrinsic
127 selectivity) of 181. The α_{H_2/N_2} of integral-asymmetric membranes can even exceed the
128 "intrinsic" value for thick films of the same polymer due to accelerated aging of the very
129 thin selective skin layer compared to thick films^{19,20,21}.

130 *Metal-decorated integral-asymmetric membranes by sputtering*

131 The membranes were sputtered on the skin side with palladium or platinum metal
132 using a DESK II magnetron sputter (Denton Vacuum, Moorestown, NJ, for 9 seconds at
133 45 mA, 100 mtorr) and were re-tested for their gas transport properties after sputtering.

134 These sputtered membranes are here also referred to as metal-decorated. The gas flux of
135 the membranes is generally reduced after sputtering as can be expected due to coverage
136 of some high-permeability polymer membrane area with a low permeability metal layer.
137 Gas selectivities after sputtering also change depending upon among other factors the
138 initial $\alpha_{\text{H}_2/\text{N}_2}$ (representing the quality of the asymmetric polymer membrane), the extent
139 of coverage of the membrane surface with metal, and the possible modification of the
140 membrane polymer skin layer itself by the sputtering plasma^{22,23}.

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

150 **Hydrogenation setup and procedures**

151 The metal sputtered membrane was installed in a stainless steel 47 mm filter
152 holder (model XX4404700, Millipore Corp., Billerica, MA) and the metal catalyst was
153 then reduced by purging H₂ over the skin side (60°C, 15 hours). Soybean oil was then
154 circulated from a nitrogen-blanketed reservoir vessel over the skin side (metal decorated)
155 of the membrane using a gear pump (Series GA, Micropump Inc., Vancouver, WA;
156 25 g oil/min) with temperature and pressure monitoring and control. Details of the

157 experimental setup are provided elsewhere ¹³. UHP hydrogen was supplied from the
158 porous substructure side of the membrane at the required pressure after the desired
159 reaction temperature was attained. The oil side pressure was always maintained at 10 psi
160 above the H₂ pressure by blanketing the oil reservoir with N₂ to prevent mechanical
161 damage (blowout) since the skin side of the membrane was not supported.

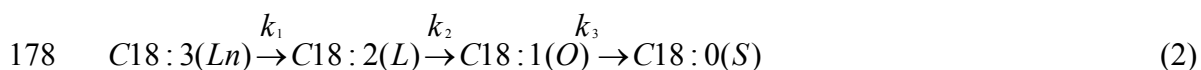
162 **Analysis**

163 Oil samples were converted to fatty acid methyl esters (FAMES) following
164 American Oil Chemists Society (AOCS) official method Ce 2-66 (alternate, ²⁴). FAMES
165 were analyzed by gas chromatography (GC, 100m CP-Sil 88 column, Hewlett-Packard
166 6890 series gas chromatograph). AOCS official method Ce 1h-05 was followed for the
167 analysis of fatty acids (Injection port and column 250°C and 181°C, respectively, He
168 carrier gas 1 ml/min, split ratio 1:100). The extent of hydrogenation is represented by its
169 Iodine Value (IV) which is the mass of iodine in grams that is consumed under standard
170 conditions by 100g of a lipid². The IV of hydrogenated oil was calculated from the
171 composition obtained by GC analysis using equation (1)²⁵.

$$172 \quad IV = (\%C16:1 \times 0.9502) + (\%C18:1 \times 0.8598) + (\%C18:2 \times 1.7315) + (\%C18:3 \times 2.6152) \quad (1)$$

173 **Hydrogenation selectivity S**

174 Hydrogenation of natural oil such as soybean oil is quite complex due to the
175 number of components present in the oil. Selectivities are calculated here by assuming
176 first-order reactions as presented in Equation 2 ². The hydrogenation selectivities can
177 then be calculated using the experimental composition data from our experiments²⁶.



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

$$181 \quad S_{Ln} = \frac{k_1}{k_2} \quad (3)$$

$$182 \quad S_L = \frac{k_2}{k_3} \quad (4)$$

$$183 \quad S_i = \frac{\Delta trans}{\Delta IV} \quad (5)$$

184 The simplified definition of hydrogenation selectivities assumes the absence of positional
185 selectivity, equal rates of fatty acid isomers, absence of any shunt reactions, and identical
186 dependence of different fatty acids on hydrogen concentration. This simplified approach
187 of calculating hydrogenation selectivities is widely accepted by fat chemists².

188 **Results and Discussion**

189 Partial hydrogenation of soybean oil was performed at 50-90°C and 50-200 psig
190 H₂ pressure using Pd and Pt sputtered integral-asymmetric polymer membranes (see
191 Table 1 for membrane properties and experimental conditions). It should be noted that
192 the H₂ pressure is applied to the porous substructure of the asymmetric metal decorated
193 membranes. The hydrostatic pressure on the skin (oil-) side of the membrane always
194 exceeds the H₂ pressure to prevent membrane blowout. This was done with a nitrogen
195 blanket on the oil circulation reservoir.

196 The hand-cast membranes studied here have a range of hydrogen fluxes J_{H_2} and
197 selectivities α_{H_2/N_2} depending on the skin thickness and the presence/absence of skin
198 defects that may allow some gas permeation by convection rather than diffusion through

199 the skin. A brief discussion of the effect of membrane properties on the hydrogenation
200 rate and TFA formation is provided below.

201 An earlier study in our lab evaluated platinum decorated polymeric membranes
202 having a range of hydrogen fluxes, skin defects, and catalyst loadings¹⁴. It was
203 observed that hydrogenation rates initially increase with the H₂ flux of the metal-
204 decorated membranes but then level off, indicating that an abundance of H₂ is available
205 and the process becomes limited by available catalyst sites. The H₂ flux and $\alpha_{\text{H}_2/\text{N}_2}$
206 showed little influence on TFA formation.

207 Based on our earlier work¹⁴ membranes were chosen that were known to supply
208 sufficient H₂ at the given temperature so that the supply of hydrogen is not limiting.

209 **Effect of temperature**

210 It is desirable to operate at high temperatures due to higher reaction rates;
211 however, higher temperatures conventionally also lead to increased formation of TFAs in
212 slurry reactors since the hydrogen solubility decreases with increasing temperature. This
213 section compares the influence of temperature on hydrogenation rate, cis-trans
214 isomerization and hydrogenation selectivities for membrane based and slurry based
215 catalysis under similar conditions.

216 *Hydrogenation rate*

217 Figure 3 shows the strong increase of the hydrogenation rate (represented by the
218 iodine value) with temperature using a Pd decorated polymeric membrane at 50 psig H₂
219 pressure. The hydrogenation rate was 3.4 IV hr⁻¹ at 50°C, increased to 10.4 IV hr⁻¹ at 70
220 °C, and to 22.4 IV hr⁻¹ at 90 °C. The hydrogenation rate for a Pt decorated polymeric
221 membrane was not significant at 50°C but increased to 3.6 IV hr⁻¹ at 60°C and 17.2 IV hr⁻¹

222 ¹ at 90°C. The hydrogenation rate constant for the palladium decorated polymeric
223 membrane at 50,70, and 90 °C was 0.39, 1.25, and 2.73 (kg of oil) (g of metal)⁻¹ (min)⁻¹.
224 While in the slurry reactor system using palladium as catalyst, it was 0.22 (kg of oil) (g of
225 metal)⁻¹ (min)⁻¹ at 90 °C and 50 psig ^{27,28}. The higher rate constant in the Pd decorated
226 polymeric membrane reactor system indicates more effective use of the available catalyst
227 as compared to the slurry reactor systems where mass transfer limitations and hydrogen
228 scarcity at catalyst surface lead to lower reaction rates.

229 The apparent activation energy (E_a) for hydrogenation for Pd as catalyst was
230 11.2 kcal mol⁻¹ and that for Pt was 11.7 kcal mol⁻¹. The slightly higher activation energy
231 for platinum is due to the lower activity of Pt as compared to Pd². Hsu et al.²⁸ observed
232 an E_a of 7.7 kcal mol⁻¹ for Pd catalyst in a slurry reactor. Under conditions which
233 measure only the catalytic properties, the measured activation energy should be
234 independent of the type of reactor. Lower apparent activation energies are obtained in
235 conditions where the availability of one reactant is limited. Such mass transfer
236 limitations appear to be present in the slurry reactor system reported by Hsu ²⁸.

237 *Trans fatty acid formation*

238 In a three phase slurry reactor an increase in temperature increases the rate of H₂
239 consumption, concurrent with a decrease in the supply rate of H₂ due to decreased
240 solubility of H₂ in oil. Therefore a *temperature increase for the slurry reactor* increases
241 the H₂ starvation of the catalyst and leads to *increased* TFA formation. In the metal
242 decorated polymeric membrane case, H₂ is supplied to the catalyst “on demand” with the
243 maximum rate of supply at a given H₂ pressure limited by the membrane characteristics.
244 Additionally, the permeability of H₂ through the membrane polymer PEI increases with

245 temperature with an E_a of about $3.2 \text{ kcal mol}^{-1}$ ¹⁸. If *membranes* with few or no skin
246 defects and sufficient H_2 flux are used, an *increase in temperature* should lead to
247 increased availability of H_2 at catalytic sites and thus *reduce* TFA.

248 Figure 4 supports the above argument and shows that a temperature increase does
249 not significantly change the TFA formation for the metal decorated membrane while the
250 slurry system (Pd on carbon) shows a clear increase of TFA with temperature²⁷.

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

259 *Hydrogenation selectivity*

260 The hydrogenation selectivity S describes the preference of hydrogenation of
261 polyenes over monoenes. The desirable case is if S is very high so that virtually no
262 saturated compounds are formed until almost all polyene has been hydrogenated²⁹. S is
263 sensitive to the conditions at the catalyst surface³⁰. If the availability of adsorbed
264 hydrogen on the catalyst surface is low, polyenes are preferentially adsorbed and
265 multibonded on the catalyst surface displacing less strongly bonded monoenes³¹. Thus
266 polyenes are preferentially hydrogenated. However, when the degree of adsorbed
267 hydrogen on the catalyst surface is high, a significant portion of polyenes may never

268 reach the polybonded state and thus will have an initial more weakly bonded state similar
269 to monoenes. This promotes hydrogenation of both polyenes and monoenes³¹, thus
270 decreasing hydrogenation selectivity.

271 For conventional slurry systems, an increase in temperature leads to a decrease in
272 surface coverage of adsorbed hydrogen and ultimately increases the hydrogenation
273 selectivity. The trend for metal decorated polymeric membranes is opposite to what is
274 observed in slurry systems (Table 2). The linoleic selectivity decreased almost 60% with
275 an increase in temperature from 50°C to 90°C. The linolenic and linoleic selectivity at 90
276 °C and 50 psig were 1.2 and 1.6 respectively, as compared to 1.7 and 6.1 for the slurry
277 reactor under similar conditions²⁸. The lower linoleic selectivity and its decrease with
278 the increase in temperature for palladium decorated polymeric membranes can be
279 attributed to increased hydrogen coverage of the catalyst surface at higher temperature
280 due to the high flux membranes used (59 GPU at 90 °C as compared to 12 GPU at 50
281 °C). This is also illustrated by Figure 6 where at an IV of 90, hydrogenation at 90°C
282 resulted in 25% more saturates and 20 percent less monoenes, as compared to 50°C.
283 Higher C18:3 at 90 °C than at 50 °C may also be attributed to increased availability of
284 hydrogen at 90 °C due to the high flux membrane used at 90 °C. The conditions at 50 °C
285 (lower hydrogen availability) promoted the preferential hydrogenation of polyenes
286 whereas the conditions at 90 °C promoted hydrogenation of both polyenes and monoenes,
287 thereby resulting in higher C18:3 at 90 °C for a given IV.

288 The apparent activation energies for the individual rate constants were calculated
289 from the plot of rate constants as obtained from equation 2 (Table 3). Both for palladium
290 and platinum decorated membranes, the order of activation energy was, $E_{a3} > E_{a2} > E_{a1}$.

291 However, for slurry reactor systems the activation energy for linoleate rate constants is
292 higher than that of oleate rate constants ². The different trends observed here can be
293 attributed to the higher hydrogen concentration at higher temperatures for the case of
294 metal decorated polymeric membranes. This is opposed to the case for slurry reactors
295 which experience a decrease in hydrogen availability at the catalyst surface as
296 temperature is increased.

297 **Effect of pressure**

298 In conventional slurry reactors the rate of hydrogenation depends upon the
299 concentration of hydrogen in the bulk oil⁷ which controls the catalyst's surface coverage
300 of hydrogen. An increase in hydrogen pressure increases the solubility of H₂ in oil thus
301 increasing the hydrogenation rate and decreasing TFA formation. For hydrogenation of
302 soybean oil using Pd-Al₂O₃ catalyst, Hsu et al. observed a reaction order of 0.6, with
303 respect to H₂²⁸. Other authors have observed reaction orders in the range of 0.2-1.6, for
304 palladium slurry reactors ^{32, 33}. The pressure dependencies substantially lower than
305 unity³² have been attributed to the presence of intraparticle H₂ diffusion limitations².
306 Boyes et al.³³ reported a reaction order higher than unity with Pd/C catalyst which was
307 attributed to simultaneous reaction involving more than one hydrogen molecule.

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

$$311 \quad J_{H_2} = P_{H_2} \frac{\Delta p}{l} \quad (9)$$

312 where J_{H_2} is the hydrogen flux through the membrane in cm^3 (STP) $\text{cm}^{-2} \text{s}^{-1}$, P_{H_2} is the
313 permeability coefficient, usually expressed in terms of Barrer, 1 Barrer = 10^{-10} cc(STP) cm
314 $\text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$, Δp is the H_2 partial pressure difference across the membrane in cmHg, and
315 l is the effective skin thickness of the membrane in cm. For a given membrane during a
316 hydrogenation run, the H_2 flux depends not only on the hydrostatic H_2 pressure applied to
317 the gas side of the membrane, but also on the rate of hydrogen consumption which
318 governs the partial pressure of H_2 in the stagnant oil layer near the catalyst. If dissolved
319 H_2 builds up on the oil side then the driving force for H_2 permeation will diminish which
320 represents a type of self-limiting mechanism.

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

331 *Hydrogenation rate*

332 For the Pd decorated polymeric membrane, an increase in H_2 pressure from
333 50 psig to 200 psig resulted in a minor increase in hydrogenation rate (Figure 7,
334 9.3 IV hr^{-1} , 50 psig; 10.6 IV hr^{-1} , 200 psig). The order of reaction with respect to H_2

335 pressure was 0.2 (Figure 8). The modest dependence of the rate on H₂ pressure may be
336 attributable to the insensitivity of hydrogen availability at the catalytic sites to system
337 pressure due to the already high concentration of hydrogen on the catalyst surface.
338 Clearly, any increase in H₂ pressure will thus not have as large an effect as observed in
339 conventional slurry reactors.

340 The Pt decorated polymeric membrane showed a slightly greater dependence of
341 hydrogenation rate on hydrogen pressure. The order of reaction with respect to hydrogen
342 pressure was 0.5. The Pt decorated membrane had about the same J_{H₂} as the Pd
343 decorated membrane but a much lower $\alpha_{\text{H}_2/\text{N}_2}$ indicating the presence of more defects in
344 the skin of the Pt decorated membrane. This may result in lower overall surface coverage
345 of the catalyst by hydrogen for the Pt membrane since more hydrogen will be primarily
346 supplied from mass transport through isolated defects in the membrane skin as "point
347 sources" vs. the evenly distributed transport by solution/diffusion through the skin. This,
348 in turn, can then reduce the hydrogenation rate somewhat, reflected in a reduced slope of
349 the IV vs. time trace for the Pd vs. the Pt decorated membrane.

350 *Isomerization and hydrogenation selectivity*

351 For Pd decorated membranes, the isomerization index decreased slightly from
352 0.35 to 0.28 with an increase in H₂ pressure from 50 to 100 psig. There was no change in
353 isomerization index from 100 to 200 psig H₂. For the case of the Pt decorated
354 membranes, the isomerization index remained in the range of 0.04-0.07 from 50 to 200
355 psig H₂ (Table 2). The Linoleic acid selectivities showed no change for both Pd and Pt
356 decorated membranes with an increase in pressure from 50 psig to 200 psig.

357 An increase in the H₂ pressure did not significantly impact the isomerization
358 indices since hydrogen probably was already abundant at the catalytic sites even at the
359 lowest pressure.

360 **Conclusion**

361 Metal decorated integral-asymmetric polyimide membranes were used to partially
362 hydrogenate soybean oil with minimized TFA formation in comparison with the
363 conventional three-phase slurry process. H₂ is supplied by diffusion from the porous
364 support side of the membrane emerging as dissolved gas at or near the catalytic sites on
365 the membrane skin exposed to the oil. A temperature increase was beneficial for the Pd
366 and Pt decorated polymeric membranes because the hydrogenation rate increased while
367 TFA formation remained low. This is in contrast to the conventional slurry process
368 where mass transfer limitations lead to increasing TFA formation when the temperature is
369 raised. Increasing the H₂ pressure did not significantly impact the membrane based
370 process.

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374 **Nomenclature**

375

376 $\alpha_{\text{H}_2/\text{N}_2}$ = ideal gas selectivity (ratio of normalized single gas flux of hydrogen and
377 nitrogen)

378 E_{a1} = apparent activation energy for hydrogenation of linolenic acid to linoleic acid, kcal
379 mol⁻¹

380 E_{a2} = apparent activation energy for hydrogenation of linoleic acid to oleic acid, kcal mol⁻¹
381

382 E_{a3} = apparent activation energy for hydrogenation of oleic acid to stearic acid, kcal mol⁻¹

383 J_{H_2} = hydrogen flux through the membrane, cm^3 (STP) $\text{cm}^{-2} \text{s}^{-1}$
 384 J_{N_2} = nitrogen flux through the membrane, cm^3 (STP) $\text{cm}^{-2} \text{s}^{-1}$
 385 k_1 = pseudo-first-order rate constant for hydrogenation of linolenic acid to linoleic acid,
 386 $(\text{kg of oil}) (\text{g of metal})^{-1}(\text{min})^{-1}$
 387 k_2 = pseudo-first-order rate constant for hydrogenation of linoleic acid to oleic acid, $(\text{kg of}$
 388 $\text{oil}) (\text{g of metal})^{-1}(\text{min})^{-1}$
 389 k_3 = pseudo-first-order rate constant for hydrogenation of oleic acid to stearic acid, $(\text{kg of}$
 390 $\text{oil}) (\text{g of metal})^{-1}(\text{min})^{-1}$
 391 l = effective skin thickness of the membrane, cm
 392 ΔP = hydrogen partial pressure difference across the membrane, cmHg
 393 P_{H_2} = permeability coefficient of hydrogen, $10^{-10} \text{ cc(STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$
 394 S_{Ln} = linolenate hydrogenation selectivity
 395 S_L = linoleate hydrogenation selectivity
 396 S_i = isomerization selectivity
 397

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488 **Tables**489 Table 1: Properties of membranes and hydrogenation conditions used in the study.

H ₂ flux [GPU]	Ideal gas selectivity $\alpha_{\text{H}_2/\text{N}_2}$	Temperature	Pressure, psig
<i>Catalyst: Palladium, 1.4 $\mu\text{g cm}^{-2}$</i>			
12	164	50	50
81	6	70	50
59	145	90	50
7	100	70	50-200
<i>Catalyst: Platinum, 3.4 $\mu\text{g cm}^{-2}$</i>			
4	18	60	50
10	5	70	50
46	64	90	50
7	14	70	50-200

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491

492 Table 2: Effect of temperature and pressure on hydrogenation selectivities for Pd and Pt
 493 decorated polymeric membranes.

Temperature, °C	H ₂ Pressure, psig	Linolenic Selectivity, S _{Ln}	Linoleic Selectivity, S _L	Specific Isomerization Index, S _i
<i>Catalyst: Palladium</i>				
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
<i>Catalyst: Platinum</i>				
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

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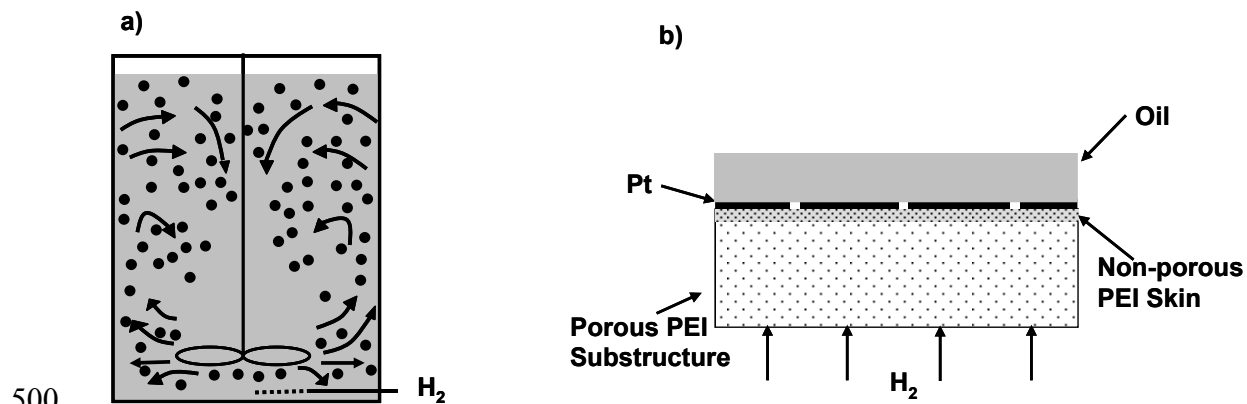
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Table 3: Activation energy

E_{a1} , kcal mol ⁻¹	E_{a2} , kcal mol ⁻¹	E_{a3} , kcal mol ⁻¹
<i>Catalyst: Palladium</i>		
7.8 (R ² =0.896)	10.0 (R ² =0.985)	15.6 (R ² =1.000)
<i>Catalyst: Platinum</i>		
10.5 (R ² =0.985)	12.3 (R ² =0.972)	13.5 (R ² =0.997)

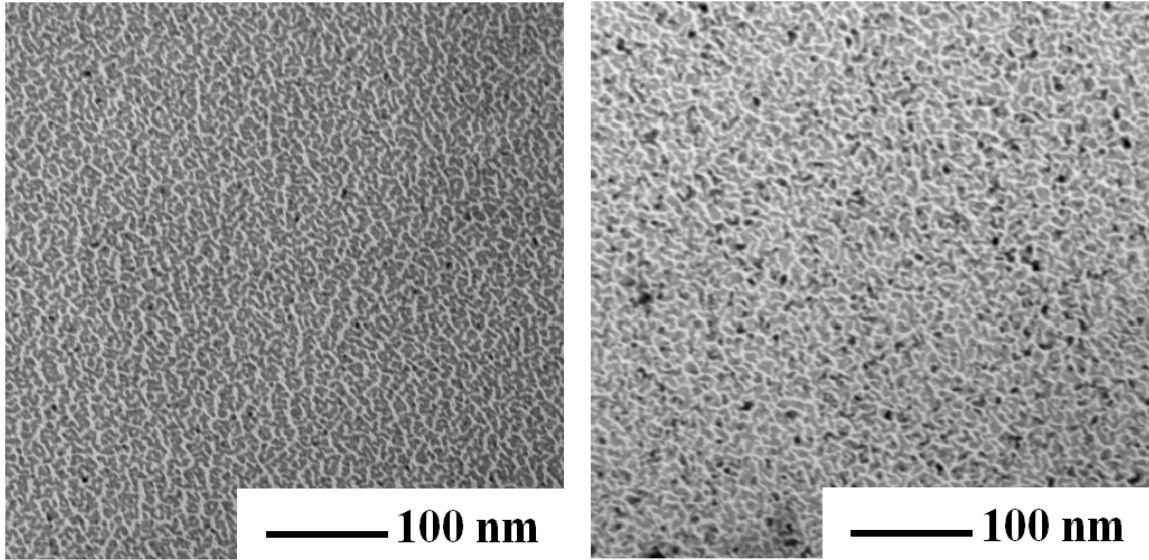
498 **Figures**

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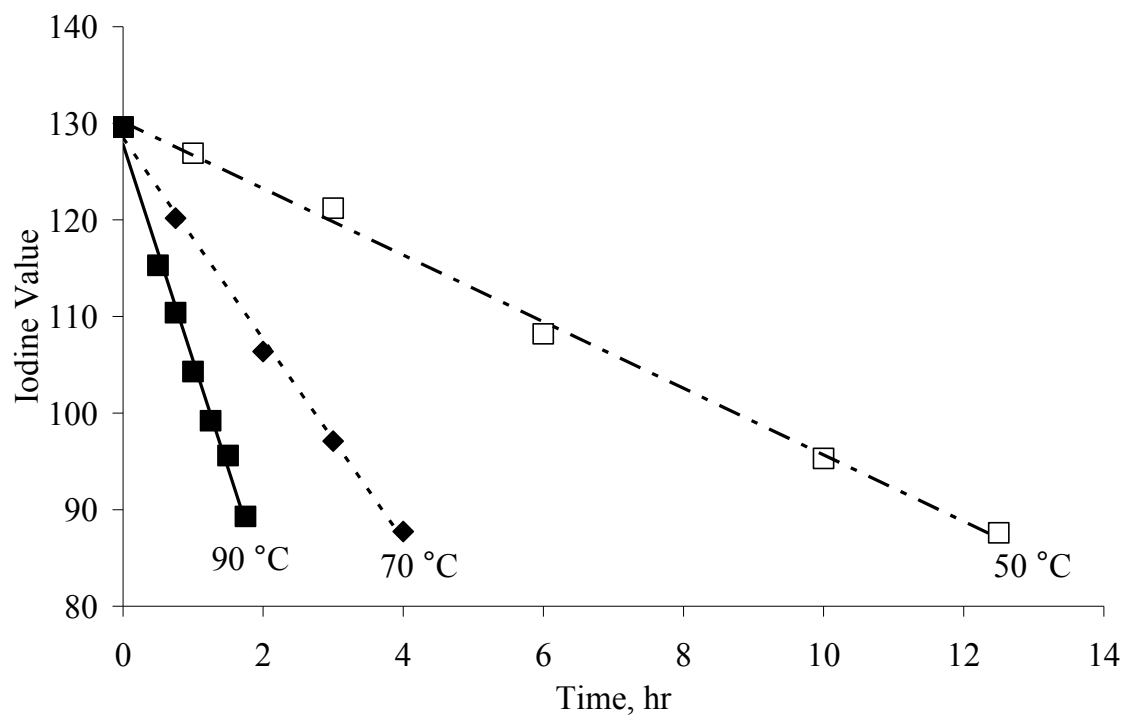
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501 Figure 1: Schematic of the conventional batch slurry reactor and the metal decorated
502 asymmetric polymer membrane reactor for partial hydrogenation of soybean oil.



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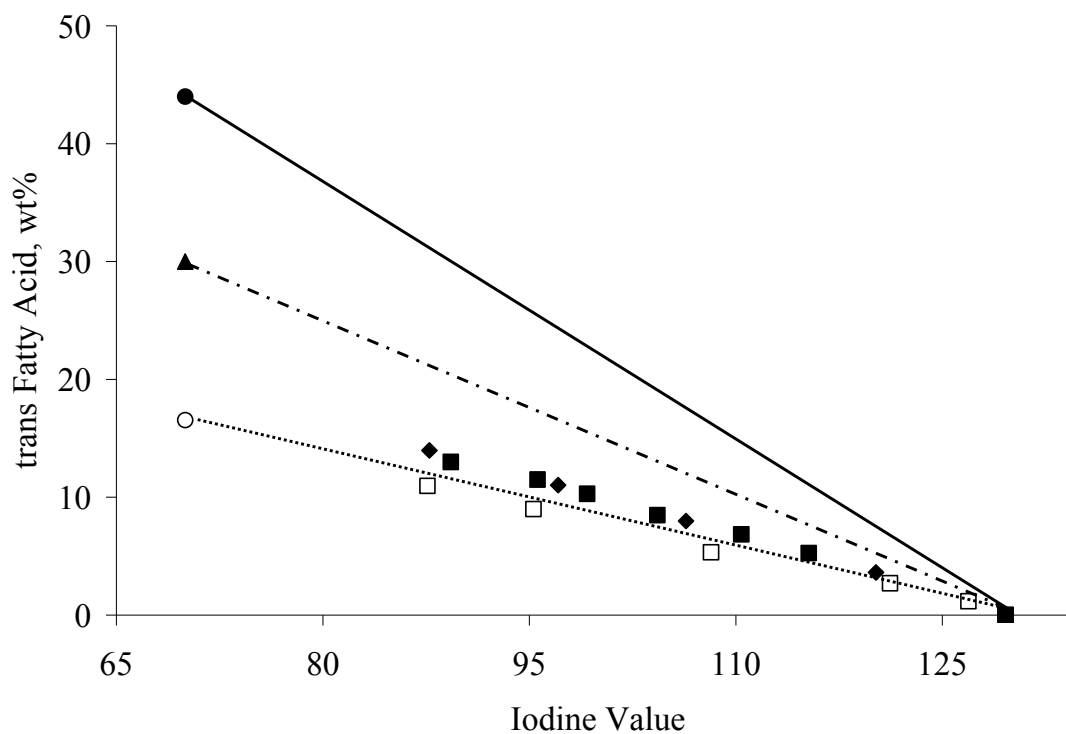
Figure 2: TEMs of the surface of PEI films sputtered with palladium (left image), platinum (right image) for 9 seconds. The images show an interconnected network of Pd/Pt islands formed at the surface of the PEI film.



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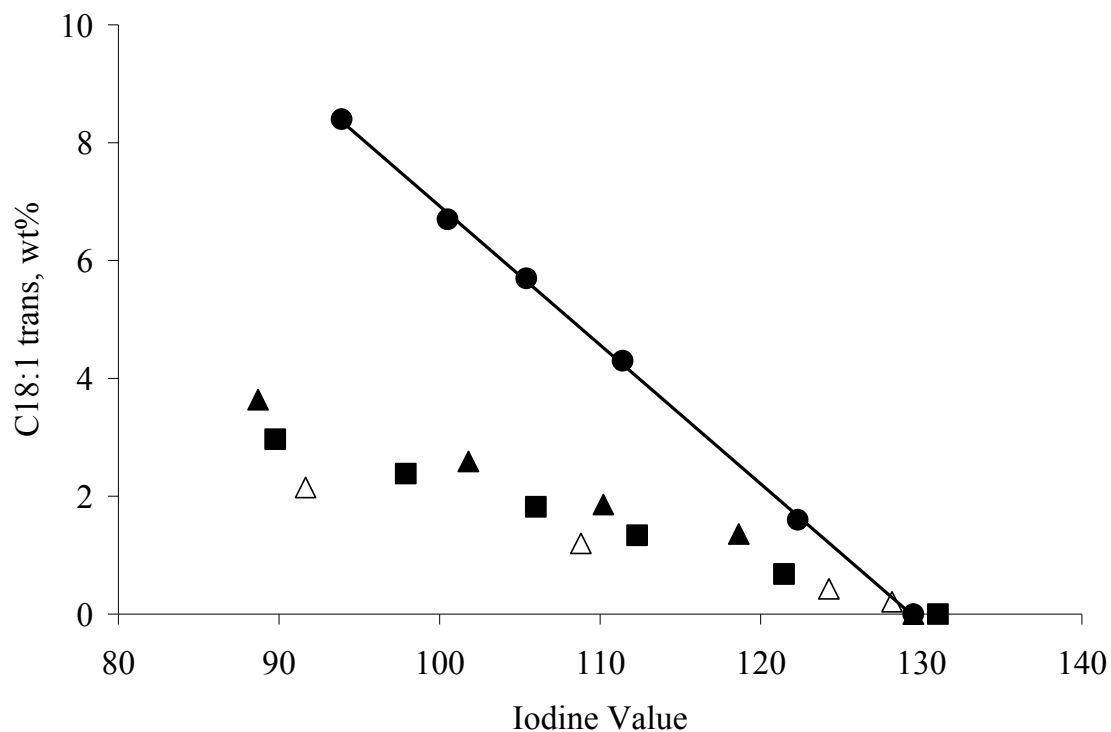
510 Figure 3: Increasing temperature accelerates the partial hydrogenation of soybean oil over
511 a palladium decorated integral-asymmetric polymer membrane.

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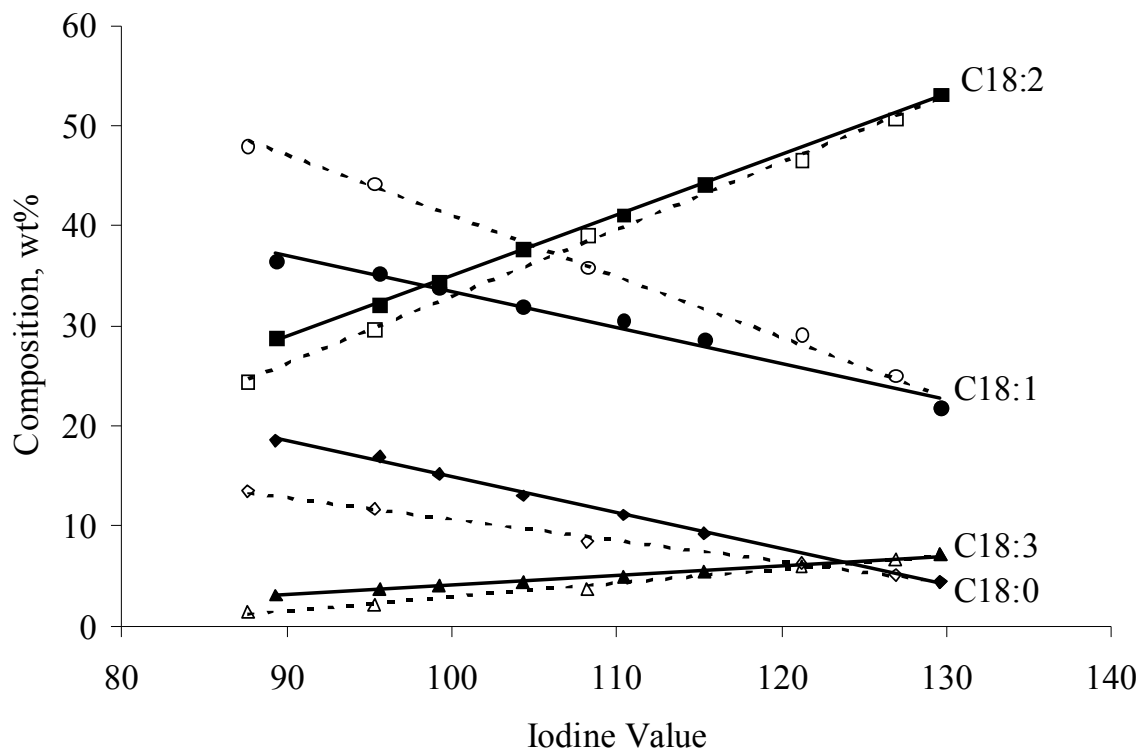
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514 Figure 4: The increase in trans fatty acid formation with temperature during partial
515 hydrogenation of soybean oil using the conventional slurry approach (Pd on alumina
516 slurry²⁴ 50°C (○), 70°C (▲), 90°C (●), lines are drawn to aid the eye and do not suggest
517 a linear relationship) is essentially reduced with the Pd decorated asymmetric polymer
518 membrane even at 90°C (Pd sputtered asymmetric polymer membrane 50°C (□), 70°C
519 (◆), 90°C (■)). This supports the notion of the high H₂ availability at the catalytic sites
520 for the membrane-based system can be effectively maintained at a variety of conditions.



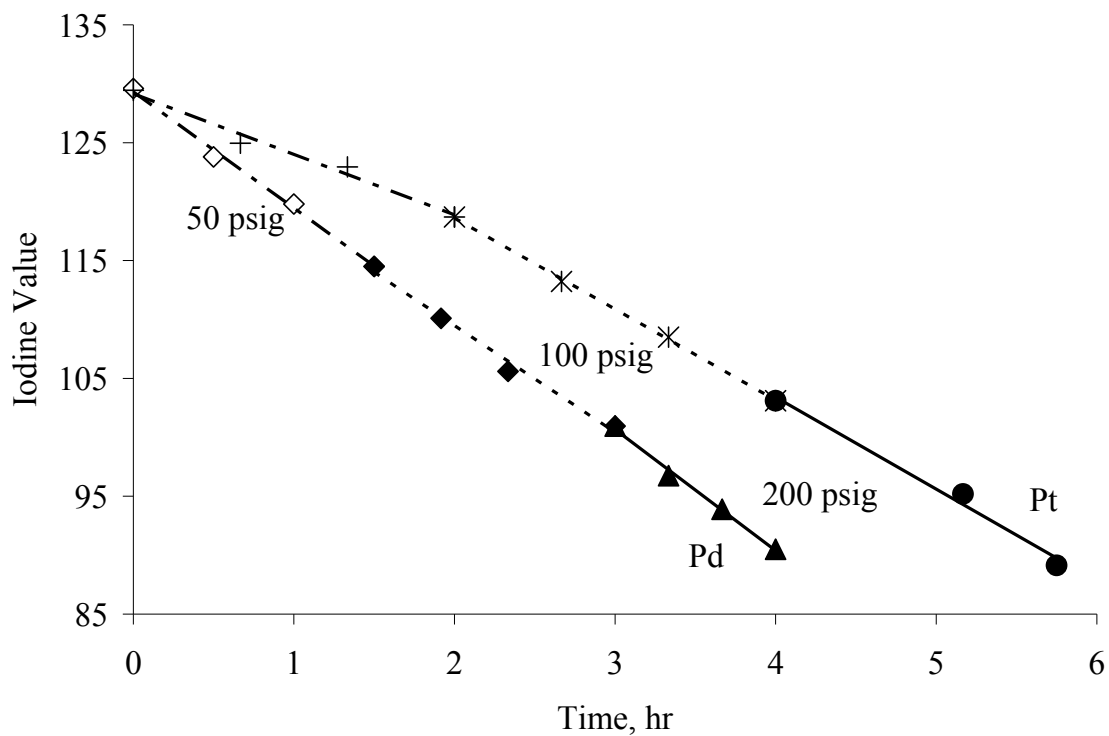
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523 Figure 5: The C18:1 trans fatty acid content increase during partial hydrogenation of
 524 soybean oil using the metal decorated polymer membranes (Pt sputtered asymmetric
 525 polymer membrane, 60°C (△), 70°C (■), 90°C (▲)) is much lower than for the slurry
 526 reactor¹³, (Pt on carbon slurry, 70°C (●)). Higher temperatures with increased
 527 hydrogenation rates can be used with the membrane approach while still maintaining low
 528 trans fat formation.



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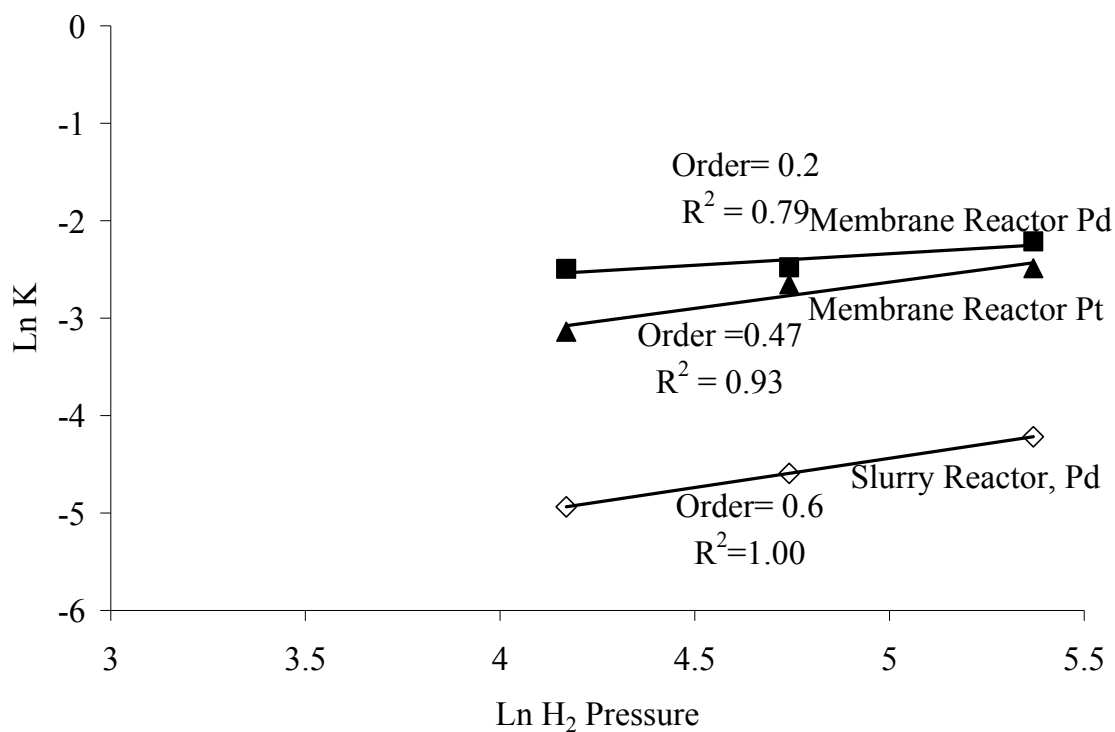
531 Figure 6: Composition profiles for hydrogenation of soybean oil using Pd decorated
 532 asymmetric polymer membranes at 50°C (-----) and 90°C (_____). Hydrogenation at
 533 higher temperatures resulted in higher saturates and lower monoenes due to possible
 534 higher concentration of hydrogen at catalyst surface at higher temperatures.



536

537 Figure 7: Effect of pressure on hydrogenation rate for Pd and Pt decorated polymeric
 538 membranes, 70°C. Pd membrane at 50 psig (\diamond), 100 psig (\blacklozenge), and 200 psig (\blacktriangle); Pt
 539 membrane at 50 psig (+), 100 psig (x), and 200 psig (\bullet). Both Pd and Pt decorated
 540 polymeric membrane reactors show a modest dependence of hydrogenation rate on
 541 pressure.

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544 Figure 8: Effect of pressure on the hydrogenation rate of a Pd sputtered and a Pt
545 decorated asymmetric polymer membrane, and Pd/alumina slurry reactor²³, all at 70°C.
546 The lower order for Pd decorated polymer membrane reactor indicates the insensitivity of
547 hydrogenation to pressure.

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