Composite catalytic tubular membranes for selective hydrogenation in three-phase systems

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0. Abstract:

Catalytic membrane contact reactors (CMCRs) were evaluated for the selective three-phase hydrogenation of the model reaction, the partial hydrogenation of soybean oil (PHSO). PHSO produces copious amounts of trans-fats when carried out in a batch slurry reactor due to hydrogen starvation at the catalyst, caused by inherent mass transfer limitations of the system. In this study composite ceramic/polymer membranes were rendered catalytically active by depositing a polymer-palladium complex, (poly(N-vinyl-2-pyrrolidone) (PVP)-palladium (Pd)), onto the selective skin of the membrane. Hydrogen gas was supplied to the support side of the membrane, the hydrogen gas permeated from the support side to the skin side of the membrane, where it dissociated onto the catalyst surface. Liquid reactant was circulated over the skin side of the membrane, allowing the three components to come into contact and react. Our system is shown to be nearly zero order in hydrogen, indicating that the catalyst surface maintains high hydrogen coverage throughout. CMCRs produced 50% less trans-fat at equivalent levels of hydrogenation compared to slurry reactors. It was further demonstrated that an increase in

temperature had minimal effects on trans-fat formation, while significantly increasing hydrogenation rates; allowing the system to capture higher reaction rates without adversely affecting product quality.

1. Introduction:

Three-phase catalytic reactions involve liquid-phase and gas-phase reactants coming into contact with a solid-phase catalyst. These three-phase heterogeneous reactions are widely used in industrial applications from pharmaceuticals to food processing. These reactions are typically carried out in batch slurry systems or trickle bed reactors. However, these traditional reactors possess inherent mass transfer limitations due to low hydrogen solubility in the liquid phase and slow diffusion to the catalyst surface. This results in hydrogen starvation at the catalyst surface, causing slow reaction rates, undesirable side reactions, or both [1, 2]. In the case of the partial hydrogenation of soybean oil (PHSO), the model reaction chosen for this study, the undesired side reaction is the production of trans-fats [3, 4].

PHSO is the process of chemically adding hydrogen to a fat molecule in the presence of a catalyst. This process converts some of the double bonds of unsaturated fatty acids to single bonds [5]. Industrial hydrogenation, or hardening, of vegetable oil has been carried out since the early parts of the 1900's [6]. Hydrogenation improves the oxidative stability, flavor stability, and changes the melting point of the oil. Unfortunately, hydrogenation also results in conversion of some *cis* double bonds to the *trans* configuration. These isomers are collectively referred to as trans-fats or trans-fatty acids. [5-7]

The accepted reaction scheme for hydrogenation of a polyunsaturated fatty acid is shown in figure 1 [7]. The scheme consists of three consecutive first order reactions in which linolenic acid is hydrogenated to linoleic acid, to oleic acid, to steric acid. This is a simplified scheme and neglects shunt reaction, isomerization, or double bond migration. The overall hydrogenation rate for vegetable oils in a dead end batch reactor has been shown to follow first order kinetics [7]. The rate constant is defined as:

$$k = \frac{\ln\left(\frac{IV_0}{IV}\right)}{t} \quad \text{Eq. 1}$$

where t is time of reaction, IV_0 is the initial iodine value, and IV is the iodine value at time t . The units of k are $\frac{1}{\text{time}}$.

Figure 1: Simplified consecutive reaction scheme for hydrogenation of soybean oil. The accepted nomenclature for lipids is expressed as $[Cx:y]$, where x is the number of carbon atoms in the lipid and y is the number of double bonds present.

PHSO reactions are typically carried out in a batch autoclave with a nickel catalyst under the following conditions: 110-190°C, 2.0-5.0 bar, and 0.01-0.15 wt% nickel [7]. These conditions are necessary to increase the solubility of hydrogen gas in the oil and to accelerate the hydrogenation reaction rate on the catalyst surface. Unfortunately, while the high reaction temperatures promote rapid reaction, they decrease hydrogen solubility in the oil resulting in low hydrogen coverage on the catalyst, and accelerate the production of *trans*-fatty acids [7].

Palladium has been widely studied as an alternative catalyst [8-11]. Palladium has an activity that is 15-20 times greater than nickel, and palladium can give lower *trans*-fat isomerization if the reaction can be run in the absence of mass-transfer limitation [11]. However, when palladium is used in place of nickel under the normal operating conditions of the latter, mass transfer limitations are known to exist and palladium produces more *trans*-fats than nickel [11].

A possible solution to overcome these mass transfer limitations, and lower the production of *trans*-fats, is the application of catalytic membrane contact reactors (CMCRs). CMCRs are created by impregnating an asymmetric membrane with a catalyst on the selective “skin” of a membrane. Hydrogen is supplied from the support side of the membrane and permeates from the support side to the skin side, where it adsorbs directly onto the metal surface. Liquid reactant is circulated over the skin side, allowing the liquid to come into direct contact with the metal coated surface of the membrane where the hydrotreating occurs (figure 2). CMCRs have the potential to eliminate hydrogen starvation by changing the transport mechanism of hydrogen delivery to the catalyst surface, thus changing the reaction from

mass transfer limited to kinetically limited. In the PHSO, the mass transfer of gas into the liquid phase is known to be the rate limiting step [7]. With CMCRs, the gas delivery to the catalyst surface is governed by the transport mechanism of the gas through the membrane: solution diffusion, Knudsen diffusion, or convection.

The system configuration shown in figure 2 is referred to as a “flow-over” system; because the liquid reactant is circulated over the surface of the catalyst. Another configuration that has received interest is the pore “flow-through” method [12]. In the flow-through configuration, catalyst is embedded inside the pores of the membrane and premixed reactants are forced through the membrane; an early name for these CMCRs was “catalytic filter” [13, 14]. By forcing the reactants through membrane pores, with either convective or Knudsen transport, excellent contact is achieved between reactants and catalyst, and pore diffusion can be eliminated as a limiting factor. We chose the flow-over system because a flow-through system is still limited by the low hydrogen solubility in the oil phase, as the oil and hydrogen must be premixed prior to flowing through the pores [15]. A study hydrogenating sunflower oil showed that this excellent catalyst-oil contact, coupled with low hydrogen solubility leads to higher trans-fat formation than a slurry reactor [15].

The concept of the catalytic membrane reactors was first introduced by Gryaznov in the 1960's [16, 17]. These early works focused on thick non-porous metal membranes. Additionally, much of the early work on catalytic membrane reactors focused on gas-phase reactions [18, 19]; while more recent work in the gas phase includes the novel destruction of chemical warfare agents [20]. Since then, CMCRs have been demonstrated using asymmetric membranes for three-phase reactions. These works include CMCRs for hydrogenation of dissolved oxygen in water [21, 22], hydrogen peroxide synthesis [23], and the hydrogenation of various vegetable oils [24]. Previous bench scale studies in our lab have shown that bench scale flat sheet membrane reactors are able to reduce the amount of trans-fats formed by up to 70% in the PHSO [25-27]. However, extending this technology from the bench scale to commercial use requires a more complete understanding of how process conditions and reactor design influences system performance.

The objective of this study was to access the potential to scale-up CMCRs for the partial hydrogenation of soybean oil. CMCRs were prepared using commercially available hollow fiber membranes. The influence of the process temperature and pressure on reaction rate and selectivity was measured. The CMCR results are compared to those of the traditional slurry system and viability for large-scale design.

Figure 2: Schematic of catalytic membrane contact reactor (CMCR). Catalyst is attached to the selective layer, hydrogen is supplied to the support side, oil is circulated over the selective layer; allowing the oil to come into contact with the catalyst.

2. Materials and Methods:

2.1 Materials

Commercial available composite tubular membranes and module (PVM-035) were purchased from Pervatech BV (Netherlands). Refined, bleached, and deodorized soybean oil (iodine value, IV = 129-132) was purchased from a local grocery store, Dillon's Food Store Inc. Poly(N-vinyl-2-pyrrolidone) (PVP) average M.W. 58,000, K29-32 and palladium(II) chloride with a purity of 99.999, was purchased from ACROS Organics™. Methanol (MeOH) 99.8% (Certified ACS Reagent Grade) was

purchased from Fisher Scientific. Hydrogen and nitrogen, ultra high purity (99.999%), were purchased from Linweld Inc.

2.2 Virgin Membranes

The membranes used are a polymeric/ceramic composite with a substrate layer of α -Al₂O₃ (outside/shell side), an intermediate layer of γ -Al₂O₃/titania, and a polydimethylsiloxane (PDMS) top layer (inside/bore side). The dimensions are 500 x 10 x 7 mm (length x O.D. x I.D.) The PDMS layer is listed as non-porous with a thickness ranging from 3 to 5 μ m.

All membranes used were flux tested using a constant-pressure variable volume apparatus as a means of quality control, a similar device is described elsewhere [28]. All flux measurements were performed at a feed pressure of 4.2 bar gauge, 0 bar gauge permeate pressure, and 25°C. The normalized gas fluxes are determined, and the pure gas selectivities ($\alpha_{i/j}$) were calculated. $\alpha_{i/j}$ is the ratio of normalized flux of pure gas i over pure gas j . Gas fluxes are reported in gas permeation units (GPU); where one GPU equals $10^{-6} \frac{\text{cm}^3_{(STP)}}{\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}}$. A membrane is considered defect free if it has an $\alpha_{i/j}$ equal to the ratio of the permeance of gas i and gas j for material of the selective skin layer (PDMS). Any skin defects in the membrane will lower this selectivity.

For this study membrane permeance and selectivities for the pure gases hydrogen and nitrogen were tested. The purpose of testing for pure gas selectivity is to probe for structural damage to the selective skin of the membrane. A small amount of skin defects were acceptable; all membranes used were required to have an $\alpha_{i/j}$ greater than Knudsen diffusion selectivity.

2.3 Catalyst Deposition

Membranes were rendered catalytically active by wet impregnation of polymer-palladium complex. A catalyst solution was prepared by dissolving 0.4g PVP and 0.2g PdCl₂ in MeOH into a 50 mL centrifuge tube and sonicated overnight in a water bath. The membranes were coated by first plugging one end of the membrane tube and filling it with 9 mL of the PVP-PdCl₂-MeOH solution. The

second end was then plugged, and the membrane was inverted several times. The membranes were drained of the PVP-PdCl₂-MeOH solution and placed in an oven at 60°C and allowed to dry for 30 min. This process was repeated five times. The coated membranes were reduced from PdCl₂ to Pd under a hydrogen atmosphere for two hours prior to use. Catalyst reduction was confirmed using powder x-ray diffraction (XRD). Because the catalyst was deposited on the inside of the membrane (diameter $\approx$ 7mm), we were unable to perform XRD directly on the membrane. Instead, reduction was performed on a model surface. A PDMS film was coated with the PVP-PdCl₂ and reduced under identical conditions; XRD was performed on this sample. The bottom two diffraction patterns in figure 3 are the unreduced PdCl₂; the bottom most pattern (—) shows pure PdCl₂ powder, the 2nd pattern from the bottom (—) shows the PDMS film coated with our PVP-PdCl₂ catalyst. The top two diffraction patterns show the reduced palladium; the 3rd pattern from the bottom (—) shows palladium on a XRD slide, and the top most pattern (—) shows the reduced PVP-Pd on a PDMS film. Both of the unreduced samples (bottom two patterns) show characteristic peaks at $2\theta \approx 17^\circ$, 27° , 28° , and 38° representing the PdCl₂ (020), (011), (120), and (111) planes respectively; these peaks are not present in the reduced samples (top two patterns). The reduced patterns shows characteristic peaks at $2\theta \approx 40^\circ$, 46° , and 67° representing the (111), (200), and (220) planes respectively. Figure 3 shows that our initial catalyst solution of PVP-PdCl₂ contains a mixture of PdCl₂ and Pd, indicating that some of the PdCl₂ was reduced prior to the deposition onto the membrane (during the catalyst solution preparation step); this is expected as methanol is known to reduce PdCl₂ [29]; however, figure 3 clearly shows that our final PVP-Pd contains no metal salt. Figure 3 also shows the amorphous halo of the PVP polymer.

Figure 3: XRD results for catalyst reduction on PDMS film model surface. XRD spectrum clearly show reduction of PdCl_2 to Pd, even in the presence of the anchoring polymer PVP. (— Additionally, the amorphous halo of the PVP is present.

Figure 4: Virgin membrane (left side) and catalytic membrane (right side). The darker color on the bore side of the membrane on the right indicates that PVP-Pd catalyst adhered to the selective layer.

Similar to Gao et al.[18], we found that the metal salt alone could not be irreversibly adhered on the polymeric skin of the membrane; however, the PVP anchored metal complex was able to adhere onto the skin of the membranes. Inductively coupled plasma (ICP) tests, at a detection limit of 5 mg/L,

performed on oil samples showed no signs of catalyst leaching into the liquid phase (ICP results not shown). Figure 4 shows that the coated membrane on the right has a darker color, indicating that PVP-Pd catalyst adhered to the selective layer of the membrane.

2.4 Reactor Set-up

A schematic of the reactor system employed is shown in figure 5. Oil is circulated through the CMCR using a positive displacement pump (Q1CSY, Fluid Metering Inc.). The recirculation loop was constructed of ¼ inch stainless steel tubing (Swagelok Company), wrapped in a heating tape (BSAT051006, BriskHeat Corporation). Hydrogen was supplied to the shell side of the reactor (support side of the membrane). Nitrogen was supplied to the oil side of the membrane; the oil side was kept at a higher pressure than the hydrogen pressure to prevent the selective skin of the membrane from being damaged.

Figure 5: Schematic of the membrane reactor setup for the PHSO experiments: (1) Piston pump; (2) membrane module; (3) membrane; (4) purge valve; (5) pressure gauge; (6) check valve; (7) hydrogen source (8) thermal couple; (9) nitrogen source; (10) sample port.

Immediately following catalyst reduction, 19.8 gram of oil was added to the system and circulated at 1 mL/sec. The system was then pressurized and purged with nitrogen, and the heating tape was turned on. Once the system equilibrated at the desired temperature, the hydrogen pressure was applied; this was recorded as the start of the reaction. 0.09g samples were collected periodically and saved for fatty acid methyl ester analysis. At the end of each experiment, the system was drained of oil and flushed with five volumes of hexane.

2.5 Sample analysis

Triglycerides were converted to fatty acid methyl esters (FAMES) using American Oil Chemists' Society (AOCS) official method Ce 2-66[30]. The corresponding FAMES were analyzed on a gas chromatogram (GC), equipped with a flame ionization detector (FID); Hewlett-Packard 6890 series. The GC method employed was AOCS official method Ce 1h-05[31]. The column used was a 100m CP-Sil 88 (Agilent Technologies), the injector port and detector were kept at 220 °C with a 100:1 split ratio, the oven was operated isothermally at 180 °C, and the carrier gas was helium at 1.0 mL per min. From the GC results, we were able to determine the iodine value (IV) of the samples using AOCS official method cd 1c-85[32].

2.6 Error Analysis:

The error bars shown represent the propagation of error present in each measurement. There were three important sources of error for the measurements reported: IV, mass of oil, and time. The error in IV (± 1.2) was determined by performing the transesterification and the subsequent GC analysis 10 times on the same sample of oil. The range from these 10 runs was used as the error in IV. The error in the total mass of oil initially charged to the reactor was taken to be ± 0.99 g. This was determined by filling and draining the system 10 times, the range from these 10 points was used. And the error in time used was ± 1.0 minute; this was the accuracy of the clocks used. These values were used to propagate the error in figures 6, 7, 8, and

9. There are two other sources of error, temperature and pressure, $\pm 1^\circ\text{C}$ and ± 0.2 bar respectively. However, these values were not used in any calculations and thus not propagated further. Temperature and pressure were usually independent variables, and errors bars were not added in the x-axis of plots.

3. Results and Discussion

3.1 Pressure effects:

The driving force for hydrogen flux across the membrane is the difference in hydrogen partial pressure between the two sides of the membrane. As the hydrogen pressure is increased on the shell side an increase in hydrogen flux and hydrogen availability at the catalyst surface is expected. As long as hydrogen consumption is greater than the ability to delivery hydrogen to the catalyst, we should expect the reaction rate to increase as the hydrogen flux is increased. However, once hydrogen delivery is greater than hydrogen consumption, the reaction rate will reach a maximum. This is indeed what we see in figure 6.

Figure 6 shows the reaction rate as a function of hydrogen pressure for the PHSO at $65^\circ\text{C} \pm 2$ using three different membranes. Each data point is a separate experiment. CMCR 1, CMCR 2, and CMCR 3 represent different membranes; however, they are structurally identical (i.e. the same catalogue number), so any variation in gas transport properties would come from variations in the manufacturing processes. The data can be divided into two regions: (1) ≤ 2 bar of hydrogen pressure, and (2) > 2 bar of hydrogen pressure. In the first region, the reaction rate increased with an increase in hydrogen pressure; however, in the second region the reaction rate remained fairly constant with increasing hydrogen pressure. In the low pressure region, the reaction is hydrogen delivery limited. Above some threshold (≈ 3 bar for this study), the reaction is kinetically limited.

The reaction order for the runs with hydrogen pressure ≥ 3.5 bar was determined to be -0.1 ± 0.2 with respect to hydrogen pressure (figure 7). This zero-order type behaviour would indicate that the

system was operating under kinetically controlled conditions and the catalyst had sufficient hydrogen coverage throughout the experiments. In contrast, a slurry system with a Pd catalyst, operating at over 50 bar hydrogen pressure, has a reaction order of 0.6 [8], indicating that the system is not operating under kinetic conditions. The reported slurry system is believed to be free of pore diffusion limitations [8], thus any hydrogen starvation must be due to low hydrogen solubility into the oil phase. Our CMCR system is able to produce kinetically controlled conditions at pressures > 4 bar, while slurry systems at pressures in excess of 50 bar are not.

Figure 6: Reaction rate as a function of hydrogen pressure for the partial hydrogenation of soybean oil at 65°C ± 2 for three different membranes. CMCR 1 (●), 2 (▲) and 3 (■) (represent different membranes; however, structurally they are identical {i.e. the same catalog number}, and with identical catalyst application). The graph shows two regions: (1) at hydrogen pressures ≤ 2 bar, hydrogen delivery limited region, where an increase in hydrogen pressure causes an increase in reaction rate, (2) at hydrogen pressures ≥ 3.5 bar, kinetically limited region, where the limiting factor is catalyst availability.

The variability in the reaction rates given in figure 6 is probably due to the lack of control in the catalyst deposition. After each experiment, the membrane was sonicated in hexane overnight, dried, and fresh catalyst was redeposit. Without a means to control the precise amount of catalyst applied for each experiment, variability in the amount and availability of catalyst is to be expected. Although CMCR 1, CMCR 2, and CMCR 3 are physically different membranes, they are treated exactly the same; the

procedures for depositing catalyst and cleaning the membranes are consistent throughout the experiments. Nevertheless, figure 6 clearly demonstrates that a CMCR can supply hydrogen sufficiently fast to achieve high and constant catalyst surface coverage that ultimately achieves fast and selective conversion.

As discussed in the experimental section, the membranes used are ceramic/polymer composites. The goal of composites is to produce a membrane that contains a very thin, selective, top layer that is supported by a nonselective porous layer [33, 34]. The ceramic layer acts as the porous support, and provides essentially no resistance to gas transport, its purpose is to provide mechanical strength to the top polymer layer. The top polymer (PDMS) layer is non-porous, approximately 3-5 μm thick, and essentially provides all of the resistance to gas transport. By minimizing the thickness of the top layer, and using a very permeable support layer, it is possible to produce a membrane that has high flux and close to the intrinsic selectivity of the selective PDMS layer [33, 34]. Which is what table 1 shows for the unmodified membranes having hydrogen fluxes between 100-300 GPU, and selectivities close to the intrinsic $\alpha_{H_2/N_2} = 2.23$ at 35°C [35].

Table 1 also shows a significant jump in hydrogen and nitrogen flux for CMCR 1 and CMCR 2 after use, while the fluxes for CMCR 3 essentially stayed constant. We believe that this is due to the repeated process of: (1) using the membranes, (2) depositing and reducing catalyst, and (3) cleaning (described above); this repeated cycle induced defects into the membrane skin. Because the selective PDMS layer is ultrathin, even small defects can lead to a large increase in gas fluxes [36, 37]. CMCR 1 and CMCR 2 were exposed to this cycle 14 and 10 times (respectively), while CMCR 3 was only used 4 times; with more uses, we expect CMCR 3 to also see an increase in flux. Table 1 also shows the selectivities of the unmodified vs. modified membranes, the selectivities can provide insight into the nature of the type of defects that are being created in the membranes.

The selectivities are between the intrinsic selectivity of PDMS (2.23 at 35°C [35]) and Knudsen selectivity (3.74). This would indicate the induced defects are small; in Knudsen range or smaller. If the defects were large, then the gas transport would be convective flow and the membrane would become

non-selective i.e. α_{H_2/N_2} would become 1. Knudsen diffusion occurs when the pores are smaller than the mean free path of the gas. When this is the case, the gas molecules will have collisions with the walls of the pores more frequently than with other gas molecules [36]. The α_{H_2/N_2} for Knudsen diffusion is

$\alpha_{H_2/N_2} = \sqrt{\frac{MW_{N_2}}{MW_{H_2}}}$, where MW_{N_2} and MW_{H_2} stand for the molecular weight nitrogen and hydrogen, respectively [36].

Figure 7: Reaction order with respect to hydrogen pressure equals -0.1 ± 0.2 , for data points ≥ 3.5 bar from figure 6 (kinetically limited region). This zero order behavior indicates that the catalyst surface maintains high hydrogen coverage throughout the experiments.

Table 1:

Membrane flux at 25°C and 4.2 bar: prior to metal deposition and after completion of reactions.

	Virgin membranes (permeance, GPU)			After reaction (permeance, GPU)			
	N ₂	H ₂	$\frac{H_2}{N_2}$ selectivity	Number of Reactions	N ₂	H ₂	$\frac{H_2}{N_2}$ selectivity
CMCR 1	32.8	113.7	3.5	14	350	1160	3.3
CMCR 2	107	263	2.5	10	550	1760	3.2
CMCR 3	88	220	2.5	4	93	196	2.1

3.2 Temperature effects:

In a traditional slurry reactor, an increase in temperature increases the rate of hydrogen consumption at the catalyst, while simultaneously decreasing hydrogen solubility in the liquid phase. These factors lead to a decrease in hydrogen coverage on the catalyst and a corresponding increase in trans-fat production [7]. Figure 8 compares the trans-fat formed, for equal levels of hydrogenation ($IV \approx 115$), as a function of the reaction temperature. A slurry reactor with a Pd/Al₂O₃ catalyst shows a significant increase in trans-fat as temperature is increased [9]. However, for the CMCR system, the production of trans-fat is essentially temperature independent. Additionally, the CMCR's trans-fat formed at all tested temperatures is less than the trans-fat formed at 23 °C for the slurry reactor. This allows the CMCR system to be operated at high temperatures, capturing higher reaction rates without adversely affecting product quality.

Figure 8: Trans-fat formation as a function of temperature. Trans-fat formation is essentially temperature independent using membrane reactors. The slurry reactor (■) show a significant increase in trans-fat formation as the temperature increases. Membrane reactors (●) operated between 2-5 bar hydrogen pressure, slurries were 3.5 bar [9]

3.3 Kinetics:

Albright [38] developed the kinetic equations for the reaction scheme shown in figure 1. The governing equations are:

$$[Ln] = [Ln_0] e^{-k_1 t} \quad \text{Eq. 2}$$

$$[L] = [Ln_0] \left(\frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) + [L_0] e^{-k_2 t} \quad \text{Eq. 3}$$

$$[O] = [Ln_0] \left(\frac{k_1}{k_2 - k_1} \right) \left(\frac{k_2}{k_3 - k_1} \right) (e^{-k_1 t} - e^{-k_3 t}) - \quad \text{Eq. 4}$$

$$[Ln_0] \left(\frac{k_1}{k_2 - k_1} \right) \left(\frac{k_2}{k_3 - k_2} \right) (e^{-k_2 t} - e^{-k_3 t}) +$$

$$[L_0] \left(\frac{k_2}{k_3 - k_2} \right) (e^{-k_2 t} - e^{-k_3 t}) +$$

$$[O_0] e^{-k_3 t}$$

Where $[Ln_0]$, $[L_0]$, and $[O_0]$ are the starting wt% of linolenic acid, linoleic acid, and oleic acid respectively. $[Ln]$, $[L]$, and $[O]$ are the wt% of linolenic acid, linoleic acid, and oleic acid at time (t). The individual rate constants (k_1 , k_2 , k_3) were calculated by solving for the three simultaneous equations above.

The temperature dependence of the rate constants are correlated using the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad \text{Eq. 5}$$

where k is the rate constant, A is the preexponential factor, E_a is the apparent activation energy, R is the gas constant, and T is the temperature in kelvin. The E_a of a reaction can be determined by carrying out the reaction at different temperatures and plotting the $\ln(k)$ versus $1/T$. The resulting Arrhenius plot will have a slope equal to $-E_a/R$. These plots were used to determine the apparent activation energy for the over rate of hydrogenation (k), and for the individual rate constants (k_1 , k_2 , and k_3); denoted as:

E_a = apparent activation energy for the overall rate of hydrogenation (k)

E_{a1} = apparent activation energy for linolenic acid to linoleic acid (k_1)

E_{a2} = apparent activation energy for linoleic acid to oleic acid (k_2)

E_{a3} = apparent activation energy for oleic acid to steric acid (k_3)

The apparent activation energy for overall (E_a), and the individual reactions (E_{a1} , E_{a2} , and E_{a3}) for our CMCR system were determined. The system was filled with oil and operated as described above (section 2.4) at four different temperatures. Four samples were taken at each temperature. After the forth sample at a given temperature, the hydrogen pressure was turned off and the temperature was increased. The system was allowed 30 minutes to equilibrate to the new temperature and hydrogen pressure was reapplied. This was repeated for the final two temperatures (figure 9). The Arrhenius plots for CMCR system was graphed and the apparent activation energies were determined (table 2).

Figure 9: Partial hydrogenation of soybean oil at four temperatures for a catalytic membrane: 50°C (◆), 60°C (●), 70°C (■), 80°C (▲). The overall and individual rate constants (k , k_1 , k_2 , k_3) were determined as well as the apparent activation energies (E_a , E_{a1} , E_{a2} , E_{a3}).

Because activation energy of a catalyst should be system independent (absent of mass transfer limitations) we compared the E_a of our CMCR to that of a slurry system. We found that the results for the CMCR system compares similarly to a slurry reactor with Pd/alumina, 36.4 kJ/mol compared to 30.1 – 35.9 kJ/mol respectively (table 3) [8]. Additionally, the Arrhenius plots for both systems were linear. The agreement of apparent activation energies and linearity of the plots would indicate that both systems are free of mass transfer limitations. However, the CMCR system achieved this at 4 bar hydrogen pressure compared to 51 bar for the slurry. This further demonstrates the ability of CMCRs to operate in the kinetically controlled region at greatly reduced pressures.

3.4 Selectivities

When hardening soybean oil, the aim is to hydrogenate linolenate (Ln, C18:3), while maintaining linoleate (L, C18:2), and minimizing stearate formation (S, C18:0). These preferences are expressed as the linolenate (S_{Ln}) and linoleate (S_L) selectivities [7, 38]. These selectivities are defined as:

$$S_{Ln} = \frac{k_1}{k_2} \quad \text{Eq. 6}$$

$$S_L = \frac{k_2}{k_3} \quad \text{Eq. 7}$$

The apparent activation energy for individual hydrogenation steps show that $E_{a1} > E_{a2} > E_{a3}$ (table 2). This is consistent with literature for both nickel [7] and palladium [7-9, 11] slurry reactors. This is credited to preferred adsorption of the polyenes over the monoenes [39]. This increasing activation energy means that it is advantageous to run the reaction at higher temperatures, as the higher temperatures will improve selectivities (figure 10). Because $E_{a1} > E_{a2} > E_{a3}$, as the temperature is increased, k_1 will increase at a greater rate than k_2 , and k_2 will increase at a greater rate than k_3 . According to equations 6 and 7, this results in higher S_L and S_{Ln} at higher temperatures, as demonstrated in figure 10. Because increasing temperatures in a slurry reactor causes an increase in trans-fats, slurries are forced to choose between improved selectivities or lower trans-fats. Membrane reactors are not forced to choose between this tradeoff; CMCRs can run at higher temperatures without the increase in trans-fats, allowing them to capture the improved selectivities.

Table 2: Summary of apparent activation energies for the CMCR

	Apparent Activation Energy (kJ/mol)	R ² of Arrhenius plot
E_a (Overall)	36.4	0.9484
E_{a1} (Ln → L)	46.9	0.9503
E_{a2} (L → O)	43.9	0.9835
E_{a3} (O → S)	28.9	0.9995

Table 3: Apparent activation energy: Membrane systems, and slurry systems

System	H ₂ Pressure (bar)	Temperatures (°C)	Ea (kJ/mol)
CMCR	4.0	50-80	36.4
Pd/alumina[8]	51.7	50-110	30.1 – 35.9

Figure 10: *Temperature effects on selectivities for CMCR. As the temperature is increased, both the S_{Ln} (▲) and S_L (■) selectivities increase. Higher selectivities are desired as S_{Ln} represents the selectivity of polyunsaturated fats over monounsaturated fats. And S_L represents the selectivity of monounsaturated fats over saturated fats.*

3.5 Scale-up

The membrane and module combination were chosen for three reasons, they are: (1) commercially availability, (2) available in the hollow fiber configuration, and (3) several module sizes were available. When accessing the scale-up feasibility of using membrane reactors on a commercial scale, commercial availability is important as this allows for easy and cheap replacement of key components. The hollow fiber configuration is important, as this is the most efficient configuration for membrane packing density[40]. We chose the smallest module available (one tube, 0.005 m² membrane surface area), and have used its performance as a basis for estimation of a pilot CMCR system for the PHSO. Ray [9] reported that 600 mL of oil, at 12 IV/hour, with 0.004% Ni loading, was an acceptably fast reaction rate for the PHSO. Extrapolating our data of 22 mL of oil, at 4.2 IV/hr, with 0.005 m² surface area for the CMCR, we would require 0.39 m² to equal the slurry's space time yield (assuming reaction rate is constant with scale-up).

When using a CMCR, all of the catalyst is attached to the surface of the membranes, thus, the amount of catalyst that a reactor can contain is limited to the available surface area of the membrane.

Whereas, with a slurry reactor, there is no limit to the amount of catalyst that can be used. This can lead to large amounts of required surface area if the reaction rate is slow; the example used above would require 0.39 m^2 of surface area. However, if the temperature can be increased without adversely effecting selectivity, as we demonstrated above, then the reaction rate can be increased while simultaneously lowering the membrane surface area required. Commercially treatment of 5-20 tonnes of oil for an IV reduction of 40 points in 8-10 hours is standard. To accomplish this using current technology would require $1500\text{-}7300 \text{ m}^2$. This could be realized in one to a few hollow fiber modules[40].

4. Conclusion

It was demonstrated that a Pd-PVP complex could be attached to commercially available membrane for use as a CMCR. The partial hydrogenation of soybean oil was used as model reaction in comparison to three phase batch slurry reactor to investigate mass transfer limitations of the gas phase delivery to the catalyst surface. It was found that at hydrogen pressures as low as 2 bar, CMCRs are able to maintain a high level of hydrogen coverage at the catalyst, with a reaction order of (-0.1 ± 0.2) with respect to H_2 pressure. This allowed our system to produce significantly less trans-fat than a slurry reactor (12 wt% vs. 30 wt% trans-fats at equivalent temperature and extent of reaction). Additionally, trans-fat formation for our CMCRs is essentially temperature independent, contrary to slurry reactors which show a clear correlation between increased temperature and increased trans-fats. Kinetic studies were performed and the E_a for the overall rate of hydrogenation of the system was found to be 36.4 kJ/mol at 4 bar hydrogen pressure; this value is in agreement with a slurry reactor operating at over 50 bar hydrogen pressure.

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Figure captions (summary):

Figure 1: Simplified consecutive reaction scheme for hydrogenation of soybean oil. The accepted nomenclature for lipids is expressed as $[C_x:y]$, where x is the number of carbon atoms in the lipid and y is the number of double bonds present.

Figure 2: Schematic of catalytic membrane contact reactor (CMCR). Catalyst is attached to the selective layer, hydrogen is supplied to the support side, oil is circulated over the selective layer; allowing the oil to come into contact with the catalyst.

Figure 3: XRD results for catalyst reduction on PDMS film model surface. XRD spectrum clearly show reduction of $PdCl_2$ to Pd, even in the presence of the anchoring polymer PVP. Additionally, the amorphous halo of the PVP is present.

Figure 4: Virgin membrane (left side) and catalytic membrane (right side). The darker color on the bore side of the membrane on the right indicates that PVP-Pd catalyst adhered to the selective layer.

Figure 5: Schematic of the membrane reactor setup for the PHSO experiments: (1) Piston pump; (2) membrane module; (3) membrane; (4) purge valve; (5) pressure gauge; (6) check valve; (7) hydrogen source (8) thermal couple; (9) nitrogen source; (10) sample port.

Figure 6: Reaction rate as a function of hydrogen pressure for the partial hydrogenation of soybean oil at $65^\circ C \pm 2$ for three different membranes. CMCR 1 (●), 2 (▲) and 3 (■) (represent different membranes; however, structurally they are identical {i.e. the same catalog number}, and with identical catalyst application). The graph shows two regions: (1) at hydrogen pressures ≤ 2 bar, hydrogen delivery limited

region, where an increase in hydrogen pressure causes an increase in reaction rate, (2) at hydrogen pressures ≥ 3.5 bar, kinetically limited region, where the limiting factor is catalyst availability.

Figure 7: Reaction order with respect to hydrogen pressure equals -0.1 ± 0.2 , for data points ≥ 3.5 bar from figure 6 (kinetically limited region). This zero order behavior indicates that the catalyst surface maintains high hydrogen coverage throughout the experiments.

Figure 8: Trans-fat formation as a function of temperature. Trans-fat formation is essentially temperature independent using membrane reactors. The slurry reactor (■) show a significant increase in trans-fat formation as the temperature increases. Membrane reactors (●) operated between 2-5 bar hydrogen pressure, slurries were 3.5 bar [9]

Figure 9: Partial hydrogenation of soybean oil at four temperatures for a catalytic membrane: 50°C (◆), 60°C (●), 70°C (■), 80°C (▲). The overall and individual rate constants (k , k_1 , k_2 , k_3) were determined as well as the apparent activation energies (E_a , E_{a1} , E_{a2} , E_{a3}).

Figure 10: Temperature effects on selectivities for CMCR. As the temperature is increased, both the S_{Ln} (▲) and S_L (■) selectivities increase. Higher selectivities are desired as S_{Ln} represents the selectivity of polyunsaturated fats over monounsaturated fats. And S_L represents the selectivity of monounsaturated fats over saturated fats.