Title: Aqueous Phase Hydrogenation of Levulinic Acid using a Porous Catalytic Membrane Reactor

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Abstract

Membrane reactors offer an alternative approach for conducting three-phase heterogeneous chemical reactions. The membrane acts as a liquid/gas phase contactor, while also serving as the support for a solid catalyst. A significant benefit from this approach is circumvention of gas phase dissolution and diffusion in the liquid phase to reach catalytic sites. This method of gas phase mass transfer allows a significant reduction in operating pressure compared to traditional three-phase reactors that often require higher gas pressures due to low gas solubility and diffusivity in the liquid phase. The membrane reactor in this work consists of a porous expanded polytetrafluoroethylene (ePTFE) membrane with deposited Ru catalyst particles. The reaction studied is the aqueous phase hydrogenation of levulinic acid to produce γ -valerolactone. The highly hydrophobic PTFE material provides an almost impermeable barrier to the liquid phase while allowing hydrogen gas to freely transport through the pores to reach catalytic sites located at the liquid/membrane interface. The reaction kinetics displayed by the membrane reactor favorably compare to those of a packed bed reactor (PBR). In terms of hydrogen pressure the maximum catalytic benefit in comparison to the PBR is obtained at pressures greater than 0.7bar, and a more pronounced and continuously increasing catalytic benefit is obtained with increasing temperature.

Keywords:

- 1.) Membrane reactor
- 2.) Three-phase hydrogenation
- 3.) Levulinic acid
- 4.) Phase-contacting membrane
- 5.) Noble metal integrated membrane

6.) PTFE porous membrane

Graphical Abstract

1. Introduction

1.1. *Membrane reactor background*

As global demand for oil grows and reserves lessen, alternative sources for sustainable fuels and chemicals are needed. Biomass based feedstock offers a sustainable alternative, but conversion possibilities and technologies must be further realized to offer practical and economically viable sources of production. Catalytic membrane reactors afford an alternative and potentially more efficient method for performing three-phase heterogeneous chemical reactions. Traditional three-phase reactors often present mass transfer limitations, namely relatively large diffusional distances to reach catalytic sites exacerbated by low gas solubility in the liquid phase. Hydrogen availability at the catalytic sites is often the rate limiting step for hydrogenation reactions [1]. Membrane reactors can alleviate the inherent mass transfer limitations by directly and abundantly supplying gas to the catalytic sites located on the membrane surface, which acts as a gas/liquid phase contactor, and thus lessen the necessity for higher gas phase pressures.

Traditional three-phase reactors may be homogeneous or heterogeneous, and examples of both include trickle-bed, fixed-bed, slurry, stirred-tank, and bubble-column [2-4]. Membrane reactors have the advantage of being heterogeneous, thus eliminating the need for catalyst separation. The catalyst phase of the membrane reactor may be integrated onto the surface or distributed/impregnated throughout the entire membrane. Excellent reviews on membrane reactors, their history and development, and their applications in catalysis and separations have been written by Vankelecom [5], Vital and Sousa [6], Dittmeyer [7], and Gryaznov [8]. In our work the membrane functions as a liquid/gas phase contactor with the utilized catalyst located at the liquid/membrane interface where the hydrogen permeates through the membrane to reach the catalytic sites.

There are some examples of hydrogenation reactions in membrane reactors in the literature on a variety of reactions, but most notable are the differences in the location of the catalyst particles and the

intended transport of the substrate for hydrogenation, as shown in Figure 1. The methods of substrate transport include: (A) diffusion in the dense membrane layer, (B) convective flow through membrane pores, or (C) convective cross-flow contact with the catalytic active surface of the membrane, as in our work. Works demonstrating the use of the membrane in the dissolution method (A) and pore flow method (B) can be found in [9, 10] and [11, 12], respectively. The surface contact method (C) is demonstrated when convective cross-flow of the liquid phase substrate across the catalytically active surface of the membrane occurs, while hydrogen, with a much higher permeability in the membrane material, is supplied from the opposite side. Examples of this method are seen in the work performed on the partial hydrogenation of soybean oil [13-15] and the removal of dissolved oxygen from water [16].

Our work is best described as method (C) where a porous, yet highly hydrophobic polytetrafluoroethylene (PTFE) membrane was used to maintain an aqueous liquid phase on one side of the membrane while allowing hydrogen to permeate and reach ruthenium catalyst on the liquid phase surface. The surface contact method of membrane reactor function is advantageous for our aqueous phase hydrogenation system, because the separation of the gas and liquid phases allows the interfacial catalyst particles to be in simultaneous proximity with gas phase hydrogen and the liquid phase organic reactant. In contrast, the dissolution (A) and pore flow (B) methods of membrane reactor function still operate with liquid phase dissolved hydrogen. The low solubility and slower diffusion of hydrogen in the liquid phase are thought to no longer be rate limiting constraints in the surface contact (C) method of operation, thus allowing far lower hydrogen pressures to be utilized in comparison to (A), (B), and other traditional three-phase reactors.

Figure 1 - Membrane reactor methods of flow and catalyst contact. (A) indicates dissolution of substrate species A and hydrogen in the membrane undergoing reaction with the homogeneously dispersed catalyst in the membrane bulk. (B) indicates a liquid solution containing dissolved substrate species A and hydrogen that undergo hydrogenation as they pass through the pores of the membrane that contain the catalyst. (C) indicates the membrane acting as a liquid/gas phase contactor with the catalyst coated on the liquid phase surface of the membrane. Hydrogenation reaction occurs as hydrogen permeates the membrane and reaches the catalytic sites.

1.2. Levulinic acid hydrogenation background

The reaction studied in this work was the aqueous-phase hydrogenation of levulinic acid using ruthenium as a catalyst, as shown in Figure 2. Levulinic acid is derived from the acid-catalyzed hydrolysis of cellulose proceeding through the reaction pathway of glucose, 5-hydroxymethylfurfural (HMF), to levulinic acid (LevA) [17-20].

Figure 2 - Levulinic acid hydrogenation to gamma-valerolactone

Levulinic acid is considered a “Top 10” biobased platform chemical and several approaches to its chemical transformation can be found in the literature [21]. Although several catalysts, supports, and solvents have been investigated for the hydrogenation of levulinic acid, many researchers agree that ruthenium is the most effective noble metal catalyst for its aqueous phase hydrogenation [22-27].

The extensive range of reaction conditions, catalyst supports, and catalyst location (heterogeneous vs. homogeneous) make a direct comparison challenging, but most literature either directly or indirectly cites mass of gamma-valerolactone (GVL) produced per unit of time per mass of catalyst. This value is usually termed catalytic rate or sometimes described as catalytic ‘productivity’ and ranges from the order of one to about one thousand depending on the system. However, two of the short-comings of describing the catalytic rate in this manner include the use of catalyst mass rather than available catalyst or number of catalytic sites, and the lack of normalizing for temperature and pressure. Nevertheless, it does allow a first approximation to comparing the various catalytic systems.

To facilitate comparison of this membrane reactor work to a more traditional reactor system, the discussion section will make frequent mention and comparison to the work of Abdelrahman, Heyden, and Bond [22]. These authors provided extensive work on reaction kinetics for the aqueous-phase

hydrogenation of levulinic acid to gamma-valerolactone in a packed bed reactor (PBR) utilizing ruthenium on carbon support. The reason for making such a comparison is to highlight the benefits of the membrane reactor in terms of hydrogen delivery and availability to the catalyst, when temperature and catalyst mass are kept the same in both cases. It is noted that in the following sections any reference to PBR data or calculations is directly referring to the aforementioned work of Abdelrahman, Heyden, and Bond [22]. Another reference is available in the literature that used a packed bed reactor with Ru/C for the aqueous phase hydrogenation of levulinic acid [28]. However, less data over the temperature and pressure ranges used in our work was presented, and they actually reported slightly lower catalytic rates for GVL production than that of [22] under the same conditions. The focus of our work was to demonstrate that a phase-contacting membrane reactor can produce higher hydrogenation rates than traditional three-phase reactors in a low pressure range (0.7 to 5.6bar) where the traditional reactors suffer from limited hydrogen availability or hydrogen starvation. This effect of hydrogen starvation actually becomes more pronounced as temperature is increased in traditional reactor systems, because the liquid phase solubility of hydrogen decreases. Whereas, conversely, the phase-contacting membrane reactor bypasses this limitation by directly supplying hydrogen from the gas phase to the catalytic sites, thus offering greater benefit at higher temperatures.

2. Materials and Methods

2.1. Materials

Tetratex expanded polytetrafluoroethylene (ePTFE) membrane material was purchased from Donaldson Company with 0.05 μ m nominal pore size and 25 μ m thickness. Matrimid 5218 powder was purchased from Huntsman Advanced Materials and used as received. All water used was HPLC grade purchased from Fisher Scientific. Levulinic acid (98+%), gamma-valerolactone (98%), and RuCl₃ (anhydrous, 99+%) were purchased from Acros Organics.

2.2. Catalytic membrane preparation

The ePTFE membrane was either used as received (unmodified) or modified with a thin spin-coated layer of Matrimid polyimide polymer. Solutions of Matrimid dissolved in dichloromethane (DCM) of compositions 0.20, 0.60, and 1.80wt% were applied via spin-coating (750rpm/s, 2500rpm, 60s) to one surface of respective ePTFE membranes. A 0.1M solution of RuCl₃ in ethanol (0.2g RuCl₃, 10mL ethanol) was sonicated for 24h. 100 μ L of this solution was dropwise applied to the surface of a 13.8cm² section of the unmodified or Matrimid modified ePTFE membrane. The ethanol was allowed to evaporate and the metal salt was reduced by placing the coated membrane under flowing hydrogen at 150°C for two hours before use in the membrane reactor system. Reduction of ruthenium to a zero oxidation state was confirmed with XRD analysis.

2.3. TEM and SEM sample preparation and imaging

TEM imaging was performed on catalyst particles deposited on a copper grid supported Matrimid thin film. The Matrimid thin film was formed by dispensing a droplet of 0.2wt% solution of Matrimid in DCM onto a surface of water. The thin film immediately precipitated and the copper grid was gently dipped into the water and raised underneath the film resting on the surface of the water. The deposited film was allowed to air dry for two hours and then approximately 5 μ L of the RuCl₃ in ethanol solution was deposited onto the film. The ethanol was allowed to evaporate and the RuCl₃ coated film/grid was

placed in a flowing stream of hydrogen at 150°C for two hours. TEM was performed on a CM-100 microscope with a 100kV electron beam.

SEM samples were prepared by sputter coating the catalyst loaded ePTFE membranes with palladium.

SEM imaging and EDS analysis was performed using a Hitachi S-3500N microscope equipped with an Oxford EDS detector using an electron beam in the 5 to 15kV range.

2.4. Reactor process

The three-phase membrane reactor process used in this study is shown below in Figure 3. The system is entirely comprised of stainless steel with appropriate Swagelok and NPT fittings. The liquid phase portion is $\frac{1}{4}$ " tubing with a 40mL liquid reservoir (not shown) giving a total liquid capacity of 60mL. The pump is a lab scale Micropump gear pump operating at about 400mL/min. The membrane housing is a stainless steel membrane holder accommodating membranes with area = 13.8cm^2 purchased from Millipore and modified to accommodate simultaneous and continuous liquid and gas cross-flows on each surface of the membrane, respectively. The gas phase stream is controlled by a low-flow metering valve allowing desired flow rate and gas pressure to be achieved. The membrane reactor system can be considered to operate under differential conditions as under our highest reported reaction rate the system achieves 0.0065% molar conversion per pass of one reactor volume over the membrane.

Figure 3 - Membrane reactor process schematic. Shaded areas indicate liquid phase while white areas indicate gas phase.

2.5. Levulinic acid hydrogenation

All hydrogenation experiments were performed with a 3wt% solution of levulinic acid in water. The hydrogen reduced membrane was placed in the membrane holder and the liquid phase portion of the system was filled with 60mL of the 3wt% levulinic acid solution. The circulation pump was turned on and the system heated to the desired temperature. When the experimental temperature was reached a sample was taken and declared to be time $t=0$. At $t=0$ hydrogen cross-flow was initiated and set to the desired pressure.

In a typical hydrogenation experiment 0.2mL liquid samples were taken at regular time intervals from the sampling port indicated above in Figure 3. Liquid samples from the 'permeate' gas phase cold trap were taken at regular but generally longer time intervals depending on the rate of liquid accumulation. Samples were analyzed using standard gas chromatography methods with a GC/MS (Agilent 7890A GC, Agilent 5975C VL mass spectrometer, DB-Wax column (30m, 0.25 μ m), He carrier gas, 4 min hold at 40°C, 20°C/min temperature ramp to 240°C, 4 min hold at 240°C). Chemical identities were confirmed with mass spectra and purchased pure standards.

3. Results and Discussion

3.1. Membrane characterization

3.1.1. Gas transport

Hydrogen and nitrogen gas permeances were measured for the unmodified ePTFE membrane, ruthenium coated, and Matrimid modified membranes in a constant pressure flux measurement apparatus, and the results are shown in Table 1. Not surprisingly, the unmodified porous ePTFE exhibited the highest flux. Adding successively higher amounts of Matrimid decreased the fluxes of both gases proportionally, as was also the case when adding ruthenium to the membrane. The selectivity for hydrogen over nitrogen did not appreciably change for any of the membrane modifications and indicates a Knudsen flow regime in all cases.

Table 1 - Gas transport properties at 25°C

	N₂ Permeance (GPU*)	H₂ Permeance (GPU*)	H₂/N₂ Selectivity
PTFE, unmodified	227000	754000	3.3
PTFE, Ru coated	183000	712000	3.9
0.20wt% Matrimid	200000	675000	3.4
0.60wt% Matrimid	169000	583000	3.4
1.80wt% Matrimid	41000	144000	3.5

*GPU defined as $1 \text{ GPU} = \frac{1 \times 10^{-6} \text{ cm}^3 (\text{STP})}{\text{cm}^2 \text{ s cmHg}}$

3.1.2. Water transport

The flux of liquid water from a cross-flow with zero hydrostatic pressure differential through an unmodified ePTFE membrane was measured using the reactor system shown in Figure 3. To better simulate reactor conditions a 1.4bar permeate cross-flow of nitrogen at 10mL/min was used on the gas phase side of the membrane to collect the permeating water. The 1.4bar nitrogen stream easily penetrated the membrane and became a head pressure in the system, thus maintaining the zero hydrostatic pressure differential. The water permeate was collected over a 12h period, and the average flux is indicated in Figure 3. Although not necessarily detrimental to the intended membrane reactor function, it is important to consider the loss of water from the liquid phase retentate when making

calculations concerning the concentrations of reactant and products. In this work it is assumed that the permeation of hydrogen substantially increases with temperature, alongside that of water, so a high availability of hydrogen is still maintained at the catalyst interface despite the increased counter-flow of water.

Figure 4 - Water flux through ePTFE membrane ($A = 13.8\text{cm}^2$) as a function of temperature. A 1.4bar nitrogen cross-flow at a rate of 10mL/min was applied to the permeate side of the membrane to facilitate permeate collection.

An attempt to increase surface area, or available area for catalyst deposition, on the liquid phase side of the membrane was made by spin-coating a dilute solution of Matrimid in DCM onto the ePTFE membrane. Matrimid polymer was chosen for this because of its thermostability, chemical inertness, and maintained mechanical rigidity in the range of reaction conditions studied. As shown in Figure 5, a modest decline in water flux was observed as the weight percent of the coating solution of Matrimid was increased. It is noted, though, that in the case of the 1.80wt% Matrimid solution coating, the water flux declined by a factor of about 1.2, whereas both nitrogen and hydrogen flux decreased by a factor of about 4. There are a few possible causes for a decline in flux of both the gases and water, such as a ‘plugging’ of some of the available pores, a narrowing of the average pore diameter, or some combination of both. As described in Section 3.2.3, the additional polymer coating actually caused a

decrease in the catalytic activity of the membrane reactor, so a thorough evaluation and discussion on the reasons for flux decline is not warranted at this time.

Figure 5 - Water flux through Matrimid modified ePTFE membrane ($A = 13.8\text{cm}^2$) as a function of Matrimid coating. There is a modest water flux decline as the Matrimid coating increases. All indicated fluxes were collected at 70°C with a 1.3bar gas cross-flow at 10mL/min.

3.1.3. Membrane morphology and catalyst characterization

Unmodified and ruthenium coated expanded polytetrafluoroethylene (ePTFE) membranes were imaged using scanning electron microscopy and web-like fibers typical to ePTFE membranes were observed [29]. Membranes used in the reactor system were imaged and no apparent morphological changes compared to the unused membranes could be discerned. Energy dispersive x-ray spectroscopy (EDS) confirmed the presence of ruthenium on the top and bottom membrane surfaces. EDS is considered to give bulk elemental compositional information with the x-ray generation volume depending on the electron beam energy and with what elements the electrons interact [30]. Considering the carbon and fluorine composition of PTFE and the porous nature of the membrane, the x-ray generation volume is expected to be several μm in depth normal to the membrane surface. The PTFE membrane is $25\mu\text{m}$ thick, so the EDS information is considered to represent the bulk composition. The atomic percent composition was

determined to be 63.0, 36.2, and 0.82% for carbon, fluorine, and ruthenium, respectively. This calculates to be a ruthenium loading of $64\mu\text{g per cm}^2$ of membrane area, or approximately $880\mu\text{g}$ total Ru loading for the 13.8cm^2 PTFE membrane. SEM image examples and EDS summary information can be found in the appendix.

Evaporating 1mL of catalyst solution and measuring the mass with a gravimetric balance yielded 7.3mg of Ru, which corresponds to a loading of $59\mu\text{g/cm}^2$. Evaporating $100\mu\text{L}$ of catalyst solution onto a quartz crystal and measuring the mass with a quartz crystal microbalance yielded a total ruthenium mass of $703\mu\text{g}$, which corresponds to a loading of $56\mu\text{g/cm}^2$. A membrane with an area five times that of the 13.8cm^2 with five times the Ru coating solution was prepared to allow approximation of the Ru loading by measuring with a mass balance with 0.1mg accuracy. This method yielded a loading of approximately $90\mu\text{g/cm}^2$. The distribution of Ru particles throughout the membrane cross-section is expected to be uniform considering the catalyst coating method involved soaking the entire membrane in catalyst solution. The four independent methods of measuring the catalyst mass gave loadings of 64, 59, 56, and $90\mu\text{g/cm}^2$, so an average of $67\pm 13\mu\text{g/cm}^2$, or $930\mu\text{g}$ total Ru for one membrane, was used for all of the rate calculations in this work for the obtained membrane reactor data and the calculated PBR rates.

TEM imaging revealed the average Ru particle size to be 2-3nm. The particle size reported in [22] was 3.6nm for Ru/C. Considering the approximate surface areas, a particle size of 2nm compared to 3.6nm indicates a nearly twofold higher number of surface atoms for an equal total mass. This observation at least partially explains the 3-4 higher catalytic rates observed for the membrane reactor system compared to the PBR under equivalent reaction conditions and is more fully discussed in Section 3.2.1.

3.2. *Catalytic activity*

3.2.1. *Effect of pressure*

The effect of hydrogen pressure on catalytic rate was measured at 0.07, 0.175, 0.35, 0.7, 1.4, 2.8, and 5.6bar in the 'permeate' gas phase stream. The 0.05 μ m pore size of the ePTFE membrane allowed the hydrogen gas to easily permeate into the head space of the reactor system on the liquid phase retentate side of the membrane, thus always maintaining a zero hydrostatic pressure differential across the membrane. The vapor pressure of water did exert some additional pressure in the retentate, however at 70°C the vapor pressure of water is about 0.3bar. Considering the ranges of the pressure gauges used in the system and the oscillatory vibration of the circulatory pump, this pressure difference was difficult to discern. In fact, a slightly higher pressure on the retentate side of the membrane is beneficial for this system as the permeate side is mechanically supported by a stainless steel screen across the entire membrane area, whereas the retentate side is only secured at the perimeter with a Viton o-ring.

The experimental runs shown in Figure 6 were all conducted with the same ruthenium coated membrane (no Matrimid addition) in a continuous manner without exposing the membrane to air beginning at 0.7bar hydrogen pressure and progressively increasing in step every approximately 24 hours to the indicated pressures. The final experiment was to return the hydrogen pressure in step to 0.7bar. This allowed examination of catalytic activity over the course of the successive experiments. Within experimental error the first and last experiments at 0.7bar had identical rates indicating catalyst stability.

Figure 6 - GVL production at cross-flow hydrogen pressures ranging from 0.7 to 5.6bar. Reaction conditions: temperature = 60°C, 930µg Ru, 60mL of 3wt% LevA in water. One membrane was utilized for all of the above experiments and each pressure was tested in increasing succession from 0.7 to 5.6bar and then returned to 0.7bar for the final ~20h of experimentation to demonstrate continued catalytic activity. The (x) data points indicate the repeated 0.7bar experiment.

Figure 7 displays the calculated linear best fit rate for GVL production in the membrane reactor

alongside the calculated PBR [22] rates at the same catalytic conditions (temperature, ruthenium mass).

Figure 7 presents additional rate data for hydrogen pressures 0.07, 0.175, and 0.35bar. These

experimental runs were performed using similarly prepared membranes, but not in a continuous

manner as described for the data in Figure 6. Hydrogen pressures of 0.07 and 0.175bar were obtained

by using a diluted stream (5% H₂ in N₂) to obtain the desired partial pressure of H₂. It must be noted

that the PBR kinetics in [22] were determined over a hydrogen pressure range from 4 to 40bar, so the

calculated PBR data shown below 4bar is an extrapolation of the model. There is a clearly greater rate

for the membrane reactor over the indicated pressure range. In [22] the authors determined the PBR

reaction kinetics were established under conditions absent of mass-transfer limitations for hydrogen

pressures greater than 4bar, and using an empirically derived power-law kinetic expression ($r = k[H_2]^n$)

they determined the reaction order (n) to be 0.6 with respect to hydrogen. Assuming a similar kinetic

expression for the membrane reactor, the reaction order with respect to hydrogen calculates to be 0.4

over the pressure range from 0 to 5.6bar. The membrane reactor results are in relative agreement with the referenced PBR results and support a half-order hydrogen dependency as suggested by [22] and fractional orders reported by others investigating low temperature noble metal catalyzed liquid phase hydrogenation [31, 32].

Figure 7 - GVL rate of production as a function of hydrogen pressure. PBR calculated rate data shown for comparison. Reaction conditions same as those in Figure 6. MR ($\circ$), PBR (---). Error bars calculated using error propagation in membrane reactor measurements.

Another method of interpreting the data presented in Figure 7 can be achieved by calculating the ratio of the membrane reactor rate to the PBR rate and observing how this ratio varies as a function of pressure, as shown in Figure 8. The PBR rate expression was strictly determined in conditions absent of mass-transfer limitations, while it is yet to be determined when hydrogen mass-transfer limitations cease in the membrane reactor system. At first approximation one may assume the mass-transfer limitations become insignificant in the membrane reactor when the rate ratio becomes constant, which appears to be above 0.7bar. With all other reaction conditions being equal, including catalyst mass, catalyst dispersion and temperature, a ratio of one would indicate that both reactors are operating with an equivalent resistance to hydrogen transfer. The approximate factor of 3.5 benefit that the membrane reactor displays may be due to a few reasons, improved catalyst dispersion compared to the

PBR and/or the that the membrane reactor is operating not strictly in a liquid phase environment. The possibility of increased rate in the membrane reactor due to catalyst dispersion is not fully investigated in this work, but is certainly suggested by the smaller average Ru particle size determined by TEM analysis as discussed in Section 3.1.3. In addition, the highly hydrophobic PTFE support likely interacts with the aqueous environment differently than the carbon support in the PBR, so there may be some interaction or protection from deactivation effects caused by the aqueous solvent occurring in the membrane reactor.

Figure 8 – Ratio of membrane reactor rate to calculated packed bed reactor rate, as a function of hydrogen pressure. It is evident that a maximum rate ratio is obtained above 0.7bar of hydrogen pressure. Error bars calculated using error propagation in membrane reactor measurements.

Alternatively, or possibly in addition to the previously mentioned effects, the active catalytic sites in the membrane reactor may be present in some combination of liquid phase and gas phase environments.

This seems plausible considering the membrane reactor, which is loaded with catalyst particles throughout its entire thickness, is situated between an aqueous liquid phase and a hydrogen gas phase.

A control experiment was performed with the PTFE membrane functioning like a PBR where the H₂ was dissolved in the liquid phase that flowed across the catalyst loaded membrane surface, as depicted in Figure 9. The control results are shown in Figure 10. All reaction conditions were identical for the

membrane reactor and control experiment. The only difference being the method of H_2 delivery into the system, liquid dissolution (control) versus permeation through the membrane (membrane reactor). The order of magnitude higher rate in the membrane reactor as compared to the control experiment supports the idea that it is not merely a benefit gained from effects related to catalyst dispersion or support composition, but rather that hydrogen delivery from membrane permeation results in a higher catalytic rate compared to the liquid dissolution and diffusion of hydrogen.

Figure 9 - (L) Depiction of porous membrane situated between liquid and gas phases. Shown to visualize how dispersed catalyst particles may be located in some combination of gas and liquid environments. (R) MR (membrane reactor) control experiment performed with H_2 dissolved in liquid phase and circulated over membrane, rather than delivered through the membrane as in typical experiments.

Figure 10 - Membrane reactor, PBR, and membrane reactor control experiment rates. Reaction conditions: temperature = 60°C, 930μg Ru, H₂ pressure = 1.4bar, 60mL of 3wt% LevA in water. Error bars calculated using error propagation in membrane reactor measurements.

3.2.2. Effect of temperature

The effect of temperature on the rate of GVL production in the membrane reactor was measured over the temperature range of 50 to 90°C. These experiments were performed with four separate ePTFE membranes, but with the same amount of catalyst solution and deposition technique used in all cases. The data presented in Figure 11 show the expected trend of increased catalytic activity with increasing temperature, also giving evidence that the membrane reactor is stable over this temperature range. More specifically, the membrane is maintaining its function as a liquid/gas phase contactor without impeding the activity of the catalyst or access of hydrogen and levulinic acid to the catalyst. Often observed in polymeric systems in the presence of water or other organic species is some degree of sorption or swelling [33-35]. Also, it has been shown that the presence of metal nanoparticles can increase the swelling behavior of fluoropolymers when exposed to organic species [36]. Although PTFE is known for being highly inert under a variety of chemical and temperature conditions, these mentioned sorption studies at least suggest the possibility of some dynamics in the polymer phase as a function of temperature and chemical environment. These dynamics may in turn have some interaction

with the metal catalyst particles. However, in this work these effects did not appear to have any detriment to catalytic performance over the reported temperature range.

Figure 11 - GVL production at temperatures from 50 to 90°C in membrane reactor. Reaction conditions: hydrogen pressure = 1.4bar, 930 μ g Ru, 60mL of 3wt% LevA in water.

Figure 12 displays the observed GVL production rates for the membrane reactor and the calculated rates for the PBR. The main cause as to why the benefit of the membrane reactor is greater at higher temperatures is related to the method of transport of hydrogen from the gas phase to the catalytic sites. As discussed in Section 3.2.1 the hydrogen permeates through the porous ePTFE membrane and then directly reaches catalytic sites on the membrane surface without the need for dissolution and diffusion in the liquid phase. Considering the solubility of hydrogen in water decreases with increasing temperature and the permeability of hydrogen in the membrane increases with temperature, it is not surprising to see this synergistic effect. To make this effect more apparent, Figure 13 displays the ratio of the membrane reactor rate to the PBR rate. There is a clear linear trend for increased catalytic benefit with increasing temperature. Recalling Figure 9 and the idea that the local liquid versus gas phase environment to which catalyst particles are exposed depends on their location throughout the thickness of the membrane, it seems plausible to suggest that the number of catalyst particles

experiencing a gas phase environment increases with increasing temperature. This effect may be due to a combination of greater evaporation of water near the gas/membrane interface and higher permeability of the membrane to hydrogen.

The activation energy and pre-exponential factor for this reactive system are calculated from the data shown in Figure 14 using the empirical rate equation $r = k[H_2]^{1/2}$ as described by [22] and an Arrhenius relation for k ($k = Ae^{-E_A/RT}$). The activation energy, E_A , is determined to be 63kJ/mol and the pre-exponential factor, A , to be $3.8 \times 10^6 \text{ mol}^{0.5} \text{ L}^{0.5} / \text{g}_{\text{Ru}} \text{ h}$. These results are in agreement with those reported for the aqueous phase, Ru/C catalyzed hydrogenation of lactic acid ($E_A = 52\text{kJ/mol}$) and propionic acid ($E_A = 64\text{kJ/mol}$) [37].

Figure 12 - GVL production rates as a function of temperature for membrane reactor (○) and calculated PBR (---). Reaction conditions same as those in Figure 11. Error bars calculated using error propagation in membrane reactor measurements.

Figure 13 - Ratio of membrane reactor GVL hydrogenation rate to calculated packed bed reactor rate, or "catalytic benefit", as a function of temperature. Error bars calculated using error propagation in membrane reactor measurements.

Figure 14 – Arrhenius plot of the natural log of the apparent rate constant, k , as a function of $1000/T$ from 50 to 90°C. k is given in units of $\text{mol}^{0.5} \text{L}^{0.5} / \text{g}_{\text{Ru}} \text{h}$.

3.2.3. *Additional polymer layer on PTFE membrane surface*

The organophilic porous ePTFE was highly sorbing of the RuCl_3 in ethanol solution, thus leaving the ruthenium ions deep inside the membrane pores as the ethanol evaporated. This is not the ideal location for the catalyst as little to no aqueous solution penetrates the pores to undergo reaction, but rather reacts at the catalyst located near the membrane/liquid interface. The goal was then to apply a thin, yet dispersed polymer layer at that interface to give greater superficial area for catalyst deposition. The polymer chosen for this was Matrimid, a commercially available polyimide with high thermal and chemical stability. Reactor experiments were performed with these modified ePTFE membranes and the catalytic activity is shown in Figure 15, and summarized catalytic rates as a function of membrane hydrogen permeances are shown in Figure 16. The desired effect of increased catalytic activity was not achieved and actually lessened with increased amounts of Matrimid. This suggests that the superficial Matrimid layer did not produce greater area for catalyst deposition, but actually either completely blocked a fraction of the number of pores or reduced the effective diameter of the pores. This assumedly caused less efficient hydrogen delivery to catalytic sites or impediment of the liquid phase reactants from reaching catalytic sites. It was noticed that no delamination of Matrimid from the PTFE was evident before or after use in the reactor. Although this attempt to better localize catalyst particles near the liquid/membrane interface was not effective, it seems to be a promising area for investigation to improve catalytic efficiency, because much of the catalyst mass in the membrane reactor is not actually utilized for reaction.

Figure 15 - GVL production with additional polymer layer on catalytic surface of ePTFE membrane. Reaction conditions: temperature = 70°C, hydrogen pressure = 1.4bar, 930 μ g Ru, 60mL of 3wt% LevA in water.

Figure 16 - GVL rate of production for each Matrimid modified ePTFE membrane. Data text labels indicate Matrimid coating solution wt%, and unmodified refers to an unmodified ePTFE membrane. All membranes were coated with the same amount of RuCl₃ in ethanol solution, however the depth penetration may be different for each membrane because of the Matrimid surface addition. Reaction conditions same as those in Figure 15.

3.2.4. Membrane reactor longevity

The reactor was operated for over 200 hours continuously with one membrane to demonstrate the stability and maintained catalytic activity of the membrane reactor. The reaction was conducted at the relatively low temperature of 50°C and modest hydrogen pressure of 1.4bar to allow continuous operation without the need for added reactant and solvent to the system. Figure 17 shows a constant linear production of GVL in the membrane reactor with no significant decline in rate over 200 hours of continuous operation. The instantaneous rate (dm/dt) was calculated using a second order, centered finite difference approximation with the available GVL mass data points. Further experiments at higher temperatures and hydrogen pressures are required to verify the stability of the membrane reactor over all of the reaction conditions mentioned in this study.

Figure 17 - GVL rate of production over extended time period. Reaction conditions: temperature = 50°C, H_2 pressure = 1.4bar, Ru mass = 930 μ g, 60mL of 3wt% LevA in water, ePTFE membrane. The left y-axis shows the GVL mass production as a function of time and the right y-axis shows the calculated instantaneous rate as a function of time. This plot demonstrates the catalytic stability of the membrane reactor and suggests no loss of catalytic activity over 200 hours of continuous operation. ($\circ$) indicates GVL mass and ($\square$) indicates the calculated instantaneous reaction rate, dm/dt .

4. Conclusions

This work has demonstrated the feasibility of using a porous ePTFE membrane as a gas/liquid phase contactor with integrated noble metal catalyst for the aqueous phase hydrogenation of levulinic acid. This concept could also be extended to the hydrogenation of a variety of water soluble substrates without any modification to the membrane as long as the reaction proceeds at an appreciable rate within the current temperature limits of the membrane reactor. The method of hydrogen delivery to catalytic sites in the membrane reactor is fundamentally different than traditional three-phase reactors in the sense that it is not necessary for the hydrogen to dissolve and diffuse in the liquid phase to reach the catalyst. Instead, the hydrogen easily permeates through the pores of the membrane reaching the catalyst located at the liquid/membrane interface. The membrane reactor is shown to be more catalytically efficient than a packed bed reactor using published kinetics available for the same metal catalyst on carbon support [22]. Membrane reactor catalytic rates as a function of hydrogen pressure over the range 0.07 to 5.6bar are presented and shown to be higher than those of a PBR under similar reaction conditions with no mass-transfer limitations. Increasingly greater catalytic benefits can be obtained by operating at higher temperatures, considering the membrane becomes more permeable to hydrogen and avoids the decreasing solubility of hydrogen in water with increasing temperature. The membrane reactor was shown to be stable with no decrease in catalytic activity over 200h of operation. Future work is to include better utilization of catalyst mass in the membrane by improving localization of catalyst near the liquid/membrane interface rather than dispersed in the entire porous structure of the membrane.

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Appendix

The following Figures A1-A3 are example images of Ru loaded ePTFE membranes used in the aqueous phase hydrogenation experiments.

Figure A 1 – Ru loaded ePTFE membrane example 1 (top view).

Figure A 2 - Ru loaded ePTFE membrane example 2 (top view).

Figure A 3 - Ru loaded ePTFE membrane (cross-sectional view).

The following page is a summary report produced by the Oxford EDS software giving the carbon, fluorine, and ruthenium composition of the ePTFE membrane. This compositional information was one of four methods used to determine the ruthenium mass loading of the membrane and is discussed in detail in Section 3.1.3 "Membrane morphology and catalyst characterization".

Project 1

8/20/2015 2:24:42 PM

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 2

Standard :

C CaCO₃ 1-Jun-1999 12:00 AMF MgF₂ 1-Jun-1999 12:00 AM

Ru Ru 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
C K	0.63	63.03
F K	0.57	36.16
Ru L	0.07	0.82
Totals	1.28