



# 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  $\gamma$ -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 0.7 bar, and a more pronounced and continuously increasing catalytic benefit is obtained with increasing temperature.

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## 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

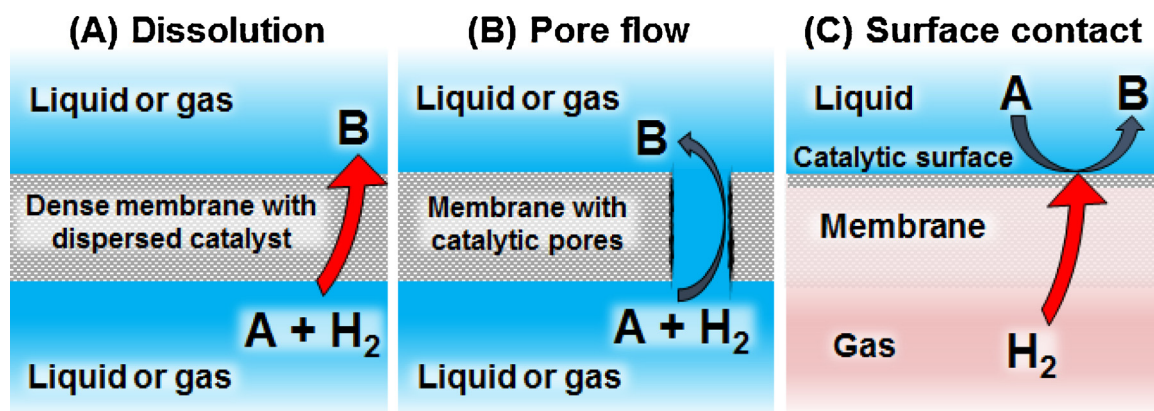
membrane surface, which acts as a gas/liquid phase contactor, and thus lessen the necessity for higher gas phase pressures.

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.

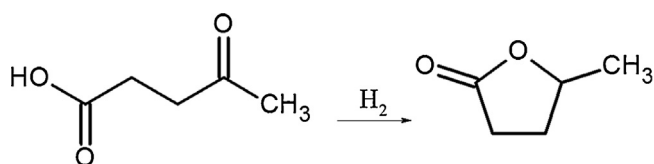
There are some examples of hydrogenation reactions in membrane reactors in the literature on a variety of reactions, but most notable are the differences in the location of the catalyst particles and the intended transport of the substrate for hydrogenation, as shown in Fig. 1. The methods of substrate transport include: (A) diffusion in the dense membrane layer, (B) convective flow through membrane pores, or (C) convective cross-flow contact

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**Fig. 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.



**Fig. 2.** Levulinic acid hydrogenation to gamma-valerolactone.

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 Ref. [9,10–12], 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.

### 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 Fig. 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].

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) makes 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 et al. [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 et al. [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 (0.7–5.6 bar) 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.

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