

Michael D Wales – Research Abstract

My research is focused on using membranes to serve as gas-liquid-solid contact zones for selective hydrogenation of model compounds. Our membrane contact reactor approach replaces the traditional three-phase batch slurry reactor. 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 causes hydrogen starvation at the catalyst surface, resulting in undesirable side reactions and/or extreme operating pressures.

Asymmetric membranes are impregnated 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 hydrogenation occurs (see figure 1). Our membrane contact reactor approach replaces the traditional three phase batch slurry reactor. By providing a contact zone for the reactants to meet, the rate limiting step, the dissolution of hydrogen into a liquid reactant, is removed. An additional benefit to the membrane reactor approach is that catalyst recovery from the hydrogenated oil is not necessary since the catalyst is immobilized onto the membrane skin.

Initially my research activities focused on the design and construction of small-scale polymeric hollow fiber modules used as reactive membrane contactors. I have experience in fiber potting and module manufacture, and have gained an appreciation for the complexity of quick-setting epoxies. More recently I began experiments using ceramic hollow-fiber membranes. In both the polymeric and ceramic cases, membrane fibers are rendered catalytically active by wet impregnation of polymer-anchored noble metals. Poly(N-vinyl-2-pyrrolidone)(PVP) is dissolved with a metal salt (PdCl_2 or PtCl_2) in water. The metal salts alone cannot be supported on the fibers; however, the PVP anchored metal complex is able to be retained on the skin of the membranes. The metal salts are then reduced in a hydrogen atmosphere. Inductively coupled plasma (ICP) tests performed on samples show no signs of catalyst leaching into the liquid phase.

Our initial model hydrogenation reaction is the partial hydrogenation of soybean oil. When operated in a tradition batch reactor, as mentioned above, there is hydrogen starvation at the catalyst; this hydrogen starvation is responsible for the formation of trans-fats. Previous bench scale studies in our lab have shown that using membrane reactors can reduce the trans-fat produced by over 50% compared to traditional reactors. My studies have focused on using hollow fibers to investigate scale-up questions. The impact of hydrogen pressure and the ratio (membrane area / reaction volume treated) on the overall performance of the system are under investigation.

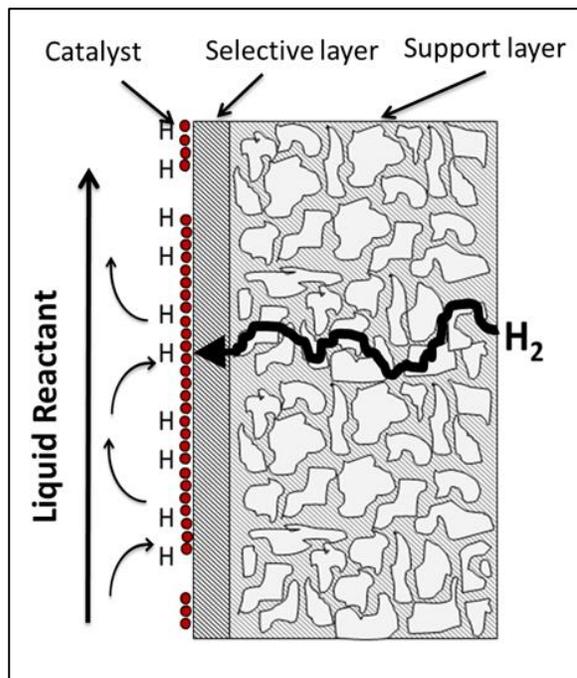


Figure 1: Schematic of asymmetric membrane used as a contact reactor

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The system is shown to be nearly zero order in hydrogen, indicating that the catalyst surface maintains high hydrogen coverage throughout the experiments. We have also demonstrated that an increase in temperature has minimal effects on trans-fat formation; allowing the system to capture higher reaction rates without adversely affecting product quality. These results would indicate that our system does not suffer from hydrogen delivery limitations to the catalyst.

Another avenue that I am investigating is different methods for catalyst deposition. In addition to the wet impregnation, I am experimenting with magnetron sputter coating. Sputter coating allows for very precise control of the amount of catalyst deposited. We have found that an increase in metal deposition on membrane reactors leads to a decrease in trans-fat formation. As with the temperature experiments, these results run contradictory to slurry reactors. In slurry reactors, increasing the amount of catalyst used causes an increase in the amount of catalyst surface area without an increase in hydrogen dissolved into the liquid. This leads to more hydrogen starvation at the catalyst, and an increase in trans-fat formation.

A second model reaction under investigation is the hydro-treating of lignin model compounds. Lignin, a byproduct of cellulosic ethanol, can be broken down into the platform chemicals benzene, toluene, and xylene (BTX) by hydrogenolysis. Conventional reactors require hydrogen pressure of 100 atm or more due to low hydrogen solubility in the liquid phase. Due to poor solvent-membrane compatibility with existing membranes, we are currently developing composite alumina-polydimethylsiloxane-polybenzimidazole (alumina-PDMS-PBI) membranes. The alumina is the support layer, PDMS acts as a gutter layer, and PBI acts as both the selective layer and interfacial layer. These are prepared through a spin coating process, with the PBI being chosen as the interfacial layer due to its chemical resistance towards aromatic hydrocarbons. We are quantifying the effects that spin speed, viscosity, and number of coats has on gas flux and selectivity.