

Catalysis in Structured Pulsed Reactors – Low- and High-Molecular Weight Hydrogenations

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Introduction

Three phase processing for many catalytic reactions often suffers from poor gas mass transfer, imperfect phase distribution, and poor solid-liquid wetting. The mass transfer process is especially complex, in that the gaseous component must first transfer to the liquid phase, then to the catalyst external surface, and finally into catalyst pores. The difficulties are more acute for viscous macromolecular solutions. One way to enhance the rate of mass transfer and improve phase distribution and wetting characteristics is to periodically oscillate the catalyst external surface between liquid-rich and gas-rich states. During the gas-rich cycle, the gas phase reactant's diffusion path is minimized. During the liquid-rich cycle, the liquid phase reactant is supplied to the catalyst and the products removed. By regulating the pulsing frequency, the surface wetting distribution can be controlled.

Reactors often used for three phase reactions include trickle beds and catalyst monoliths operated in slug flow. A problem with trickle beds is maldistribution of the downflowing liquid rivulets. Monoliths have high wetting efficiencies but cannot operate in a stable and uniform manner at the higher gas/liquid loadings characteristic of trickle beds. Previous studies have shown that pulsing the flows in trickle bed reactors can result in significant gains in activity. [1] However, trickle beds have been limited in the range of pulse frequency due to problems with pulse coalescence. [2]

Materials and Methods

Two novel pulsed reactors have been studied for the improved hydrogenation of both low- and high-molecular weight reactants. The first system is a reactive extruder where catalyst coated monoliths are placed in the exit die of a counter-rotating twin screw extruder. This reactor was used to study the hydrogenation of polystyrene (PS) to polyvinylcyclohexane (PVCH). Initially, 2-10 wt% PS was dissolved in a 10 vol% THF/ cyclohexane solution. Oscillations were recorded using a photocell. Natural extruder oscillations result due to partial screw filling, in agreement with previous work. [3] This system can also be pulsed in a forced manner by introducing additional hydrogen into the extruder barrel via an automated valve. Results were compared to a high pressure stirred tank at comparable conditions and correlated using mass transfer correlations for slug flow in monoliths. [4,5]

The second system is a vertical catalyst monolith reactor where oscillations are generated at the bottom of the monolith stack by a diaphragm attached to a piston-camshaft that can be adjusted for frequency and amplitude. This reactor is now being used to study the hydrogenation of α -methylstyrene (AMS, 15 vol% in cyclohexane) to cumene as a test of its applicability to determine intrinsic kinetics for gas mass-transfer limited reactions.

The base catalyst used for most reactions was 0.5 wt% Pd/ γ -Al₂O₃ washcoated on a 100 or 200 cpsi cordierite monolith. Typical surface area is 290 m²/g with ~70% dispersion. The support has an average pore diameter of 10 nm and a FWHM of 7 nm. The catalyst was prepared using an ion exchange method. [6] For PS hydrogenation, products were analyzed by UV spectrometry (conversion) and capillary viscometry (MW determination). AMS hydrogenation products were determined by GC.

Results and Discussion

Reactive Extrusion

The volumetric range of two-phase flow for PS hydrogenation was from G/L = 0.5 at 2.0 MPa to G/L = 1.2 at 3.5 MPa. This flow is discontinuous with pulsation, characteristic of a liquid-starved extruder. Observed rate constants were determined by modeling the system in plug flow with first order dependences in aromatic group and hydrogen concentrations, from which a pseudo first order (in aromatic group) rate constant (k_{obs}) was calculated.

This is a highly diffusion-limited process; observed reaction rates for a 10 wt% PS solution are approximately an order of magnitude less than for a 2 wt% solution at otherwise similar conditions. For 2 wt% solutions at low average liquid space velocities (0.14-0.48 mL/s/g Pd), observed rate constants ($1-3 \times 10^{-5}$ L/s/g Pd) are below those obtained from batch autoclave studies where intraparticle and liquid film diffusional resistances were minimized. However, increasing liquid and gas flow rates simultaneously increases k_{obs} in excellent qualitative agreement with correlations for the external gas-liquid mass transfer coefficient in slug flow monolith systems (Fig. 1). [4,5] The higher velocities result in a thinner liquid film surrounding the gas slug, allowing easier diffusion of hydrogen to the catalyst surface. At high flow rates (0.8-1.8 mL/s/g Pd) these rate constants are ~50% of the k_{obs} 's for an agitated vessel at comparable conditions ($\sim 1 \times 10^{-4}$ L/s/g Pd). Therefore the catalyst monoliths can be operated at high G/L almost as efficiently as an agitated vessel, for the polymeric system.

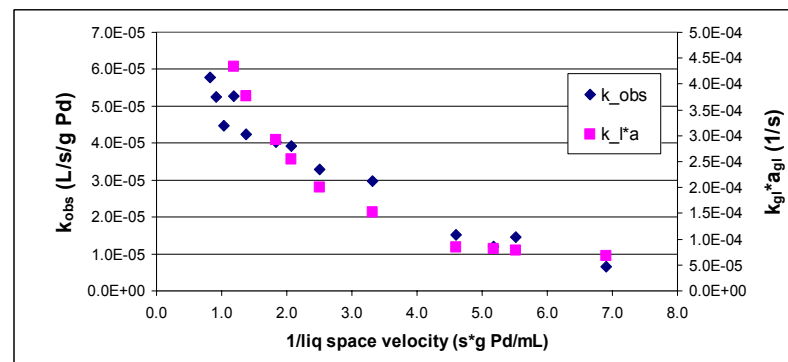


Figure 1. Data for a 2 wt% PS solution, 180 C, 3.0 MPa, no forced-pulses

Both monolith supported and powdered catalysts were run in a stirred tank at the same conditions. Identical k_{obs} ($\sim 9 \times 10^{-5}$ L/s/g Pd) were obtained for both cases, indicating that supporting the catalyst on a monolith does not alter its behavior, and that the reaction of 2 wt% PS is not internally mass-transfer limited with respect to hydrogen or polymer.

Forced pulsing was performed at frequencies around 0.1 Hz. This had the effect of adding periodic large spikes in gas slugs superimposed over the natural oscillatory flow behavior (Fig. 2). The exit distribution of these gas pulses could not be controlled, however. This is most likely due to gas back mixing in the extruder barrel and bubble coalescence. Forced pulsing showed no advantage over the natural oscillations for the 2 wt% PS system. Studies are underway to determine the effect of forced pulsing for higher (>10 wt% PS) solutions where the degree of backmixing will be less.

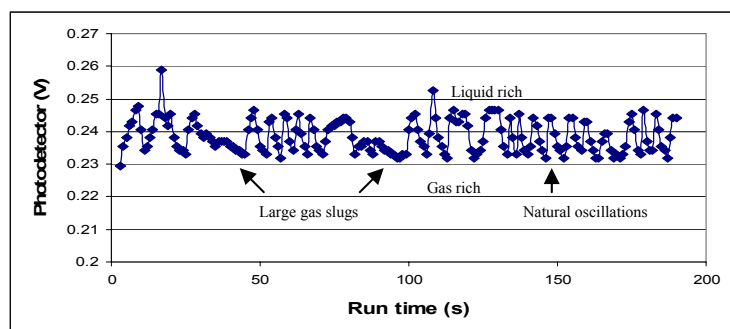


Figure 2. Photodetector voltage showing alternating liquid/gas behavior of extruder die

Oscillating Monolith Reactor

Initial mass transfer experiments were carried out at two amplitudes (1.36 mm and 2.46 mm) and at two gas flow rates (4 mL/s and 30 mL/s) for the air/water system. The results of these experiments (Fig. 3) show that for increases in either amplitude or gas flow rate the rates of mass transfer are enhanced. For example, at an amplitude of 2.46mm and gas flow rate of 30 mL/s, the rate of mass transfer is increased by up to 700% compared to results at no oscillation. When the frequency is increased to 10 Hz, the mass transfer coefficient increases gradually. Further increases in frequency result in significantly increased rates of mass transfer, which can be attributed to resonance effects that can be predicted theoretically. [7,8]

High speed photographs have confirmed that during the piston downstroke the liquid is drawn into the monolith channels and a liquid-rich condition dominates. On the piston upstroke, gas is discharged from the sparger and a gas rich condition is obtained. Studies are underway to determine the effects of oscillatory operation on AMS hydrogenation.

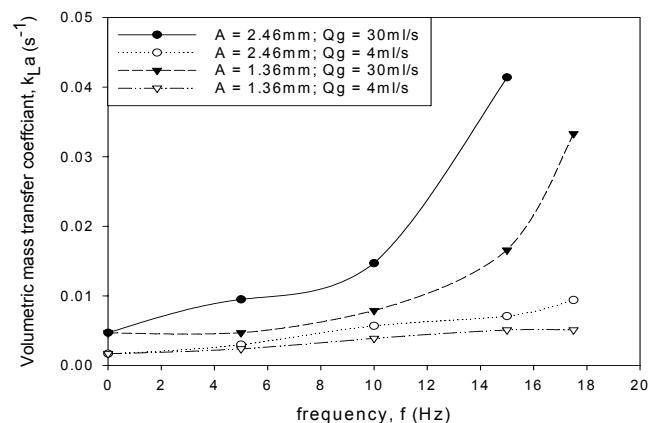


Figure 3. Volumetric mass transfer coefficient for oxygen into water as a function of frequency, flow rates, and amplitude

Significance

The improved hydrogenation of macromolecules is of particular importance industrially. Hydrogenated polymers have value as low dielectric media. This class of reactions is also applicable to bio-fuel processing and edible oil hydrogenation. The vertical oscillating monolith reactor can be used to run normally gas mass-transfer limited reactions at conditions where intrinsic kinetics can be determined, for use in catalyst screening and development.

References

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