Polymer Hydrogenation by Reactive Extrusion – Pulsed and Continuous Flow Systems

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We have modified a twin screw extruder (screw L/D = 13) to serve as a reactor for the pulsed catalyzed hydrogenation or dehydrogenation of polymers. A test reaction, poly(styrene) (PS, average MW = 100,000) hydrogenation to poly(vinylcyclohexane), is currently under investigation. The Pd-based hydrogenation catalysts are coated on cordierite monoliths housed in a square die. For example, a high dispersion 0.5% Pd/γ-Al_2O_3 was slurry coated on a 100 cpsi cordierite monolith to a thickness of ~100 μm to give a catalyst similar in activity and selectivity to those used in previous studies for the hydrogenation of α-methyl styrene.[1, 2]

The custom-made die housing the monoliths was attached to a counter-rotating twin screw extruder. The polymer solution is pumped from an autoclave, where hydrogen is pre-dissolved, to the extruder entrance, traveling the length of the extruder barrel and through the monoliths. A photocell at the die exit records the presence of gas slugs and their duration.

The volumetric range of stable two-phase flow for 2-10 wt% PS in 10 vol% THF/cyclohexane was from G/L = 7 at 2.0 MPa to G/L = 20 at 3.5 MPa. Below 2.0 MPa, there were periods of little to no gas exiting the extruder. Above 3.5 MPa, G/L did not significantly increase. Observed rate constants were determined by modeling the system in plug flow with first order dependences in aromatic group and hydrogen concentrations.[3] 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 ($1\text{-}3 \times 10^{-5}$ 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 the observed rate constants in qualitative agreement with correlations for gas-limited mass transfer in slug flow monolith systems.[4] At high flow rates (0.8-1.8 mL/s/g Pd) these approach 50% of the observed k's for an agitated vessel at comparable conditions ($\sim 1 \times 10^{-4}$ L/s/g Pd), suggesting an increase in the mass transfer rate for H_2, gas to liquid and liquid film to catalyst surface.

It is worth noting that for a liquid-starved extruder, oscillations in pressure and G/L arise naturally, with the highest frequency mode determined by screw speed (0.17 Hz in our case).[5] So these preliminary investigations were themselves pulsed, although the period of oscillation was long.

Further reaction studies are underway with the reactive extruder operating in pulsed mode at frequencies between 0.002 and 1 Hz. This is done by attaching a solenoid valve to the extruder at mid-barrel so a pulse of hydrogen can be superimposed on the steady flow rate at regular intervals. In this manner the system can alternate between gas- and liquid-rich conditions within the monoliths, oscillating the liquid film thickness to allow for rapid hydrogen mass transfer during part of a cycle. This also allows the reactor to be run under higher G/L than in steady-state operation for the same pressures. Gas slugs randomly exited the extruder at pulsing frequencies from 0.001-0.1 Hz, indicating some back-mixing in the barrel and bubble coalescence. However, higher average exit gas frequencies resulted from faster pulsing. Initial results show observed rate constants equal to or slightly higher than for runs at naturally oscillating conditions, but decreasing as the frequency approached 0.1 Hz. We are initiating studies of the same reaction in a related oscillating reactor where the pulses are controlled by a piston-cam arrangement. With this system it is possible to vary pulse frequency and pulse amplitude independently over much wider ranges than possible in a pulsed extruder.

These pulsed systems should be applicable to a broad range of macromolecular reactions, including fuels production from bio-based oils and edible oil hydrogenation. Catalyst selectivity in such serial pathway reactions (low MW hydrogenated oligomers are ultimate products) may also be improved, because pulsing in the correct frequency range can alter catalyst wetting behavior, possibly flushing intermediate product from the catalyst before an undesired reaction occurs.

References

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