

ENHANCED RATES OF GAS-LIQUID REACTIONS IN A PISTON OSCILLATING MONOLITH REACTOR

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Summary

The catalytic partial hydrogenation of soybean oil and the oxydesulfurization of simulated number 2 diesel were carried out in a novel piston oscillating monolith reactor (POMR). The POMR uses low frequency oscillations to alternate liquid- and gas-rich environments in the reactor channels of catalyst monoliths. Even application of low frequency (0-20 Hz) and amplitude (2.5 mm) vibrations results in significant increases in the observed rates of such reactions, well above what can be obtained in stirred tanks operated at equivalent power/volume ratios. A theory of oscillating transport in membranes is employed to explain the results.

Keywords: Novel reactor technologies; multiphase and particulate reactors.

Introduction

While agitated tank slurry reactors are common for many gas-liquid-solid reactions, the use of structured catalysts can obviate a catalyst separation step. Previous work on three-phase structured reactors has shown they are a viable alternative for gas mass transfer-limited reactions such as hydrogenations.^{1,2} Monolith reactors in slug flow show improved surface wetting compared to trickle beds, which suffer from rivulet formation and radial gradients in concentration at the catalyst external surface.

Improvements in trickle bed performance are possible when inducing pulsed flows, through periodic modulation of the liquid feed flow.³⁻⁶ By alternating between gas- and liquid-rich conditions over the surface of the catalyst, the gradients in the gaseous reactant's concentration can be reduced. Catalyst monolith reactors already exhibit alternating gas and liquid slugs passing slowly through the channels, approaching plug flow. Therefore, a logical extension of the pulsed trickle bed to monolith reactors is to impose forced oscillations on top of the slower natural oscillations, with a goal of further increasing the activities of gas mass-transfer limited reactions to the point where kinetic rates can be observed. Such a reactor can also be used in catalyst testing where structured catalysts are to be used but intrinsic kinetic data are required.

A piston oscillating monolith reactor (POMR) has previously been used to show activity enhancements of up to 84% and equal or better selectivity for the hydrogenation of alpha-methyl styrene (AMS) to cumene, compared to a stirred tank reactor at the same conditions.⁷ These improvements result from low frequency/amplitude oscillations that enhance external gas mass transfer to the surface, while also altering the surface wetting behavior. The liquid films are apparently reduced in thickness for at least part of the cycle. This work is an extension of the oscillating reactor system, exploring reacting systems of

higher viscosity (soybean oil hydrogenation) and characterized by more complex reaction networks (soybean oil hydrogenation and diesel oxydesulfurization) than AMS hydrogenation.

Introduction

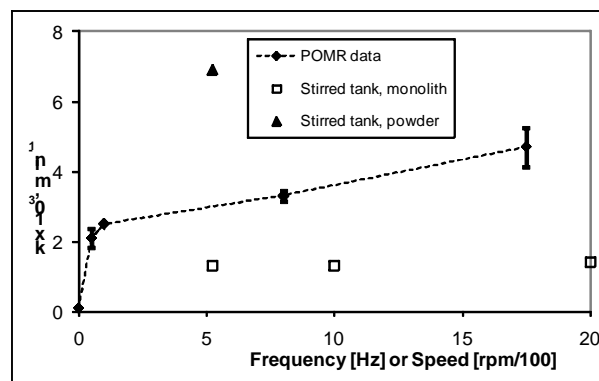


Figure 1. Effect of frequency on rate constant in the POMR, 0.5% Pd/Al₂O₃ on monolith catalyst. For stirred tank data the X-axis is agitator speed. POMR conditions: T = 110 °C, P = 0.41 MPa, A = 2.5 mm. The curve is for visualization only.

As an example of POMR operation, soy oil hydrogenation rates were measured at pulsing frequencies from 0-17.5 Hz, keeping other operating parameters constant at T = 110 °C, P = 0.41 MPa H₂. Figure 1 shows that the observed first-order (in concentration of double bonds) rate constants increase with the frequency of oscillation. Enhancements of 220% can be achieved with 17.5 Hz vibrations, as compared to no forced (piston) vibrations. The vibrations at 0.5 Hz are natural to the system (circulating pump, etc.); in the complete absence of

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vibrations the observed rate for the monolithic catalyst is near zero.

For comparison purposes, hydrogenation was also carried out in a stirred vessel using the same monolithic catalyst as in the POMR, under identical temperature and pressure conditions. From Fig. 1 it can be seen that the reaction rate in the stirred tank was substantially lower than in the POMR even without forced oscillations. These higher rates can be attributed to higher rates of both external and internal (in the washcoat) mass transfer in the POMR, as will be shown by standard calculations and measurements in the agitated tank at different speeds and with different particle sizes. Equivalent power input per unit volume (P_v) is a commonly used criterion for comparing two reactor systems. For the POMR, P_v was calculated as shown in previous work.⁸ This P_v was then used to find the corresponding agitated tank rpm at identical P_v using the correlation of Pandit et al.⁹ for a stirred tank with a marine propeller and no gas sparger. The observed k in the POMR is more than double the k in the agitated tank at equivalent P_v .

Since significant external and internal mass transfer resistances exist in the POMR, improvements in POMR performance with increasing frequency suggest that either or both resistances are decreased. Improvements in the rate of reaction due to enhancements in the external mass transfer have already been shown in our previous work,⁷ and can also be discerned from increasing k_{ov} (overall external mass transfer of H_2) values computed by several available correlations. The possibility of improving reaction rates by altering the internal transport also exists. Bakker et al.¹⁰ showed that the alternating flow of gas bubbles and liquid slugs in a monolith can enhance internal convection and diffusion in a macroporous structured catalyst. Our calculations suggest further enhancements in internal transport take place when such natural oscillations are coupled with low/frequency / amplitude forced oscillations.

Chandhok et al.¹¹ achieved up to two orders of magnitude enhancement in k_{La} with pulsating flow through a liquid membrane, at frequencies in the 1 Hz range. Leighton and McCready¹² explained that the enhancement of diffusive transport in membranes due to oscillating flows results from enhanced Taylor dispersion in the pores themselves, and that existing correlations of such dispersion can explain the quantitative enhancements observed in liquid membrane transport. Applying an analysis similar to that of Leighton and McCready, we show that the range of enhancements in our observed first-order rate constants are consistent with computed values, if a pulse penetration distance is assumed. In other words, there is both enhanced intraparticle and external mass transfer of H_2 in the soybean oil hydrogenations, and both enhancements are the direct result of the forced oscillations. The penetration distances for the pulses (down the pore

lengths) are only a fraction of actual washcoat thicknesses, suggesting that further enhancements are possible at higher pulsing amplitudes; this is being tested.

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