

Supplementary Material

(1) Germain, A. H.; Lefebvre, A. G.; Lhomme, G. A., "Experimental Study of A Catalytic Trickle Bed Reactor," Adv. Chem. Ser., **1974** (133), 164-180.

For the **slurry reactor**, the rates were computed from the regressed kinetics equation (Eq. (1) of paper) at 46°C and 0.44 MPa, for 0.5 wt% Pd/Al₂O₃. These were determined in cumene solvent (50–100 mol% AMS, zero order) at 2000 rpm stirring speed. Germain et al. demonstrated by the usual particle size and variable speed tests that the mass transfer resistances were negligible under these conditions.

Rate = 55 mmol/(s* gPd)

(2) V. Meille, C. de Bellefon, D. Schweich, "Kinetics of α -Methylstyrene Hydrogenation on Pd/Al₂O₃," IECR, 41, 1711-1715 (2002).

For the **slurry reactor**, the rates were computed from the regressed kinetics equation (Eq. (4) of paper) at 46°C and 0.44 MPa, for 1 wt% Pd/Al₂O₃. These were determined in methylcyclohexane solvent (0.5–100 wt% AMS, zero order) at 1500 rpm stirring speed. Meille et al. demonstrated by the usual particle size and variable speed tests that the mass transfer resistances were negligible under these conditions.

Rate = 460 mmol/(s* gPd)

(3) Khadilkar, M. R.; Al-Dahhan, M. H.; Dudukovic, M. P. "Parametric study of unsteady-state flow modulation in trickle-bed reactors," Chem. Eng. Sci., 54, 2585-2595 (1999).

For the **trickle bed reactor**, data were obtained at variable temperature due to heat effects (but 50°C max.) and 0.3 MPa, with hexane solvent at 1582 mol/m³ AMS, using a small diameter 0.5% Pd/Al₂O₃. The slope of the initial rate plot (conversion vs. residence time) was taken from Fig. 2 of the paper and multiplied by the initial concentration of AMS, and divided by the catalyst density and fraction of Pd to give the result.

The calculated liquid and gas superficial velocities are 0.03 and 6.6 cm/s, respectively.

Rate = 0.112 mmol/(s* gPd)

For the **pulsed trickle bed reactor**, data were obtained at similar conditions except 1484 mol/m³ AMS, with a pulse frequency of 1.7×10^{-2} Hz and a split (on flow/total flow for the liquid pulse) of 0.25. The slope of the initial rate plot was taken from Fig. 3a of the paper and multiplied by the initial concentration of AMS, and divided by the catalyst density and fraction of Pd to give the result.

Rate = 0.162 mmol/(s* gPd)

(4) A.T. Castellari and P.M. Haure, "Experimental Study of the Periodic Operation of a Trickle Bed Reactor," AIChE J, 41, 1593-1597 (1995).

For the **trickle bed reactor**, data were obtained at 41°C and 0.1 MPa, with pure AMS using a 2 mm eggshell 0.5% Pd/Al₂O₃. The rate in mmol/(gcat*s), from Fig. 2 of the paper, was divided by the fraction of Pd to give the result.

The calculated liquid and gas superficial velocities are 0.45 and 3.0 cm/s, respectively

Rate = 0.2 mmol/(s* gPd)

For the **pulsed trickle bed reactor**, data were obtained at similar conditions with a pulse frequency of 1.7×10^{-3} Hz and a split (on flow/total flow for the liquid pulse) of 0.3. The rate in mmol/(gcat*s), from Fig. 6 of the paper, was divided by the fraction of Pd to give the result.

Rate = 0.86 mmol/(s* gPd)

(5) S.K. Dhiman, V. Verma, D.P. Rao, M.S. Rao, "Process Intensification in a Trickle Bed Reactor: Experimental Studies," AIChE J, 51, 3186-3192 (2005).

For the **rotating trickle bed reactor**, the rates were measured at 40°C and 1 bar, with pure AMS. The rate for the 1% Pd/Al₂O₃ catalyst (1.5 mm spheres) was used, at rotation speed 2200 rpm, the maximum rate at the maximum rotational speed. The rate per bed volume from Fig. 5 of the paper, 40×10^{-7} mol/(cm³ bed*s), was divided by the catalyst density (1.17 g/cm³, Table 1) and by the Pd loading to give the rate in mmol/(s*g Pd).

The liquid superficial velocity for this calculation was 0.12 cm/s, approximately the highest used here. The gas flow rate was not given.

Rate = 0.34 mmol/(s* gPd)

(6) P. Cini and M.P. Harold, "Experimental Study of the Tubular Multiphase Catalyst," AIChE J, 37, 997-1008 (1991).

For the **tubular membrane reactor**, the rate was interpolated from Fig. 7 of the paper, at 46°C and 0.1 MPa, with pure AMS. This rate is in mmol/(s*g cat), which is multiplied by (100/2) to put in mmol/(s*g Pd), since there was 2% Pd on the membrane catalyst.

The computed velocities at reaction conditions are: 0.15 cm/s for liquid, 27 cm/s for gas.

Rate = 1.0 mmol/(s* gPd)

(7) H. Purnama, P. Kurr, A. Schmidt, R. Schomaker, I. Voigt, A. Wolf and R. Warsitz, “ α -Methylstyrene Hydrogenation in a Flow-Through Membrane Reactor,” *AIChE J*, 52, 2805-2811 (2006).

For the **slurry reactor**, rate data were taken from Fig. 3, for a 0.5% Pd/Al₂O₃ catalyst at 1 MPa, 53°C, >1600 rpm, 50 vol% AMS in cumene. At these conditions, Purnama et al. estimated no intraparticle or external limitations to mass transfer, and found first-order behavior with respect to H₂ pressure. At 4 MPa H₂, the rate was 4 mmol/(s*g Pd) with 80% conversion in 52 min, for the most active catalyst. For the same catalyst at 1 MPa, the conversion was 80% in 25 min, so the rate $\sim (4)(52/25)$.

Rate = 8.3 mmol/(s*g Pd)

For the **flow-through membrane reactor**, the reaction conditions are: 0.1 MPa, 40°C, 0.35 mol/L AMS in heptane, at maximum liquid flow rate. The rate was taken from Fig. 5, using the maximum rate.

The computed liquid superficial velocity is 0.37 cm/s. The H₂ was dissolved in the liquid (1600 rpm) prior to contact with the membrane.

Rate = 9.0 mmol/(s*g Pd)

(8) Abdallah, R.; Magnico, P.; Fumey, B.; de Bellefon, C., “CFD and kinetic methods for mass transfer determination in a mesh microreactor,” *AIChE J*, 52, 2230-2237 (2006).

For the metal mesh microreactor, the rate was measured at 0.28 MPa, 40°C, pure AMS, with a 1% Pd/Al₂O₃ catalyst. The observed rate in mol/(m³ liquid*s) was taken from Table 1 of the paper, multiplied by the ratio of liquid to catalyst volume (155/15), then divided by the catalyst density and the Pd loading to give the rate in mmol/(s*g Pd).

The calculated liquid and gas superficial velocities are 0.036 and 0.11 cm/s, respectively

Rate = 8.6 mmol/(s*g Pd)

(9) M.T. Kreutzer, P. Du, J.J. Heiszwolf, F. Kapteijn and J.A. Moulijn, “Mass Transfer Characteristics of Three-Phase Monolith Reactors,” *Chem. Eng. Sci.*, 56, 6015-6023 (2001).

For the monolith reactor, the rates were determined at 46°C and 1 MPa from Fig. 6 of the paper. The first-order rate constant is given, which is then multiplied by the equilibrium concentration of H₂ in the liquid to obtain an overall rate on a reactor volume basis. A hydrogen solubility in toluene of 36.5 mol/m³ was used, extrapolating from the data of Yin and Tan.

Jian-Zhong Yin and Chung-Sung Tan, "Solubility of hydrogen in toluene for the ternary system $H_2 + CO_2 + \text{toluene}$ from 305 to 343 K and 1.2 to 10.5 MPa," *Fluid Phase Equilibria*, 242, 111-117 (2006).

The liquid superficial velocity was 15 cm/s, the gas velocity 20 cm/s.

Rate = 2.1 mmol/(s*g Pd)

(10) I. Mazzarino and G. Baldi, "Liquid phase hydrogenation on a monolithic catalyst," in *Recent Trends in Chemical Reaction Engineering*; Wiley Eastern Ltd.: New Delhi, 1987; Vol. 2, p. 181.

Data were obtained at 40°C, 0.1 MPa, with no solvent – pure AMS feed.

The liquid superficial velocity is the highest used. The gas superficial velocity is 1.1 cm/s.

Rate = 0.8 mmol/(s*g Pd).