

Houston, R. W., and C. A. Walker, "Absorption in Packed Towers," *Ind. Eng. Chem.*, **42**, 1105 (1950).
Hughmark, G. A., "Heat and Mass Transfer for Turbulent Pipe Flow," *AIChE J.*, **17**, 902 (1971).
———, "Models for Vapor-Phase and Liquid-Phase Mass Transfer on Distillation Trays," *ibid.*, **17**, 1295 (1971).
———, "Momentum, Heat, and Mass Transfer for Fixed and Homogeneous Fluidized Beds," *ibid.*, **18**, 1020 (1972).
Sherwood, T. K., and R. L. Pigford, *Absorption and Extraction*,

p. 282, McGraw-Hill, New York (1952).
Vidwans, A. D., and M. M. Sharma, "Gas-Side Mass Transfer Coefficient in Packed Columns," *Chem. Eng. Sci.*, **22**, 673 (1967).
Zabban, W., and B. F. Dodge, "Effect of Total Pressure on the Gas-Film Absorption Coefficient in a Packed Tower," *Chem. Eng. Progr. Symp. Ser. No. 10*, **50**, 60 (1954).

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Direct Solid-Catalyzed Reaction of a Vapor in an Apparently Completely Wetted Trickle Bed Reactor

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Experimental evidence is presented to show that in a trickle bed reactor operating under apparently completely wetted conditions some vapor-phase reaction may be catalyzed directly by the solid catalyst at liquid flow rates typical of pilot-plant size reactors and of some industrial reactors.

EXPERIMENT

The hydrogenation of benzene at 76°C, four degrees below the boiling point, was studied in a bed of 2% Pt-on-alumina spherical pellets 0.635 cm (1/4-in.) in diameter held in a glass-walled reactor. This was maintained isothermal by automatically-controlled electrical heaters. The catalyst bed was 3.81 cm in internal diameter, 10 cm high and surmounted by a layer 3.5 cm high of inert alumina pellets, also 0.635 cm in diameter. The liquid distributor was a flat shower head with 47 pipes to provide uniform initial liquid distribution on the alumina pellets even at low liquid flow rates. Incoming benzene was preheated and saturated with hydrogen. It was assumed that the liquid and gas stream were in equilibrium with each other by the time they reached the catalyst because of the ample opportunity for contact provided by the shower head design and the inert packing. The exit gas stream from below the catalyst bed was condensed, measured, and analyzed by gas chromatography. The liquid phase was also analyzed. The mole fraction of hydrogen in the gas phase was calculated to be 0.125. Readings from five thermocouples located in the center of the inert pellet section and catalyst section showed that axial temperature gradients were less than 0.1 to 0.2°C. The maximum temperature difference radially between the center of the bed and the wall was less than 1°C.

Before each run reported, the reactor was heated to 120° to 140°C under H₂ flow for at least two days, then cooled to room temperature and heated up to reaction temperature under an automatic control system all under H₂ flow. Only then was benzene introduced into the system. The conversion was a fraction of 1% at all times so the reactor can be treated as a differential reactor. The superficial hydrogen flow rate was 0.146 cm/s (S.T.P., inlet conditions) although the total of H₂

plus benzene vapor flow rate was about 1.17 cm/s (again, S.T.P., inlet conditions). More details are given by Özel (1973).

RESULTS AND DISCUSSION

Table 1 summarizes the results of three runs of interest, each at a different liquid flow rate. In Run 1 the feed contained some cyclohexane; in the other two the feed was pure benzene. The figure shows, for Run 2, the typical change in concentration with time of the exit gas and liquid phases until steady state was reached. At all three flow rates studied the exit gas phase concentration exceeded that in equilibrium with the liquid phase and both concentrations decreased to steady-state values reached only after a period of 1 to 2 hours. The steady state rate of reaction also decreased with increased flow rate. At the highest liquid flow rate, Run 3, there was little change in liquid exit composition with time, but the gas phase concentration dropped from 4×10^{-3} mole % at 30 min. to the steady state value of 1.1×10^{-3} mole % after about 90 min. Analysis was by gas chromatography.

By running very dilute solutions of cyclohexane in benzene over inert spherical alumina pellets in the reactor at 76°C in the presence of H₂ the mole fraction ratio y/x was found to be constant at 1.6 for the range of concentrations obtained. In each case the amount of gas phase condensate agreed well with that corresponding to the vapor pressure of benzene at 76°C. Although the composition difference between the two phases is striking, the mass flow rate of liquid is so much greater than that of the vapor that most of the cyclohexane formed, for example, 95% for run 2, left in the liquid phase.

Calculations (Özel, 1973) showed that mass transfer limitations were substantial. For the three runs, γ was estimated by the stagnant film model to be about 0.6 to 0.7 and the internal effectiveness factor varied from about

TABLE 1. EXPERIMENTAL RESULTS

Run no.	Liquid flow rate, g/cm ² (s)	Liquid feed conc., mole %	Liquid prod. conc., mole %	Vapor condensate conc., mole %	Vapor conc. in equil. with liquid product	Liquid react. rate, g-mol (s) (cm ³ of cat.)	Superficial liquid vel., L, cm/s	Liquid Reynolds no., $\frac{d_p L \rho}{\mu}$
1	0.0874	4.5×10^{-4}	1.9×10^{-3}	8.2×10^{-3}	3.04×10^{-3}	8.2×10^{-9}	0.11	15.8
2	0.1967	0	5.7×10^{-4}	2.18×10^{-3}	9.1×10^{-4}	7.2×10^{-9}	0.24	35.7
3	0.3034	0	3.1×10^{-4}	1.1×10^{-3}	5.0×10^{-4}	6.1×10^{-9}	0.37	55.0

* All values refer to steady state conditions.

0.07 to 0.09. Visually all catalyst pellets appeared to be wet. Wet pellets were easily distinguishable from dry ones due to their very dark colors, visible from the outside of the reactor. Moreover, when the reactor was filled with alumina pellets (0.4 cm diam.) which become transparent when wetted with benzene, it was observed that all the beads were wetted.

Careful observations through the glass-walled reactor during and in the absence of reaction showed that the liquid flowed downwards in rivulets which tended to maintain their position with time. Some catalyst pellets were thus covered with a trickling liquid film while others, although wet, were without a liquid film on the surface. During the start-up period, catalyst pellets in the second category slowly became dark so that probably they were becoming wetted by a capillary effect from adjacent pellets. Presumably this group of pellets provided the mechanism for direct solid-vapor contact. Nonuniformity of the liquid flow in trickle bed reactors has been reported previously, but it is worth noting that this occurred here at liquid Reynolds numbers, $d_p L \rho / \mu$, as high as 55 and in spite of the extreme measures taken to provide initial uniform distribution of liquid. On any one pellet, the film fluctuated in thickness in a regular manner (with a cycle time of several seconds at the lowest flow rates), but the film seemingly never disappeared completely. The amplitude of fluctuation decreased at higher liquid flow rates, approaching continuous film-like flow at the highest liquid rate.

The amount of cyclohexane found in the exit gas stream sets only a lower limit to the amount formed by direct vapor-catalyzed reaction since transfer of cyclohexane from the vapor phase to the liquid phase occurs simultaneously with reaction. Using the correlation of Petrovic and Thodos (1968) to estimate a gas-liquid mass transfer coefficient and assuming that gas and liquid reaction rates are each constant with position in the reactor, one can calculate, for example, for Run 2, that as much as a third of the cyclohexane in the exit liquid stream could have formed in the gas phase and then transferred to the liquid phase in the reactor. However, such a calculation is sensitive to the value of the mass transfer coefficient taken and assumptions concerning where the gas-solid catalyzed reaction actually takes place, and this result is approximate. The overall steady state conversion, expressed as g-mol/(s) (cm³ of cat.), dropped by about 25% when the liquid flow rate was increased three-fold, and the ratio of the exit vapor concentration to that in equilibrium with the liquid also dropped as liquid flow rate was increased, as shown in Table 1. Both observations indicate that vapor-phase reaction was considerable, that liquid-phase reaction was substantially diffusion-limited, and that the ratio of vapor-phase to liquid phase reaction decreased, as would be expected, with increased liquid flow rate.

Liquid superficial velocities as used, for example, in various trickle bed reactors in petroleum refining vary greatly, from typically about 0.17 cm/s (20 ft/hr) for relatively heavy feedstocks (high viscosity and b.p.) to ten or more times that value for light gas oils and naphthas. For a 6.1-m (20-foot) long reactor these figures translate into values of the liquid hourly space velocity (LHSV) of 1 to 10 or more. Scale-up in industry is usually done on the basis of constant LHSV and since laboratory-scale or pilot plant reactors are usually much shorter than commercial-sized reactors, superficial liquid velocities are correspondingly less. For a 0.6-m long reactor equivalent liquid superficial velocities become 0.017 to 0.17 cm/s (2 to 20 ft/hr). The liquid superficial velocities studied here are at the high end of the scale of values expected to be encountered in bench scale reactors simulating commercial petroleum practice. Our highest liquid flow rate is about the same as the lowest encountered industrially.

PREVIOUS STUDIES

There are few other studies with which to compare the above observations and the two we cite below used much lower liquid flow rates than did we. Under these conditions the catalyst may be very slow to become fully wetted and may indeed operate in an incompletely wetted fashion even after steady state conditions are reached. A well documented case is the study of Sedricks and Kenney (1972) of the hydrogenation of crotonaldehyde at 30°C and atmospheric pressure over 0.476 cm × 0.476 cm (3/16 in. × 3/16 in.) pelleted palladium-on-alumina catalyst. Most of their studies were at a superficial liquid flow rate of 0.0045 cm/s. (The superficial hydrogen flow rate at the inlet was 0.57 cm/s, calculated at S.T.P.) Even at steady state, wetting was incomplete but was improved by surrounding the pellets with 8 to 16 mesh inert granules and became apparently complete if this second arrangement was preflooded. The rate of reaction decreased with time up to several hours and also with increased liquid flow rate. The rate of reaction was shown to be much slower on wetted pellets than on dry pellets because of severe diffusion limitations on the former. The decrease with time was explained by gradual seepage of liquid into the pores of initially unwetted pellets. Qualitatively these results are similar to ours except that under steady state conditions our bed appeared to be completely wetted.

Hartman and Coughlin (1972) studied the catalytic oxidation of SO₂ by air in a countercurrent trickle bed reactor in which water ran down over a bed of carbon particles (at superficial velocities of from 4.3×10^{-4} to 6.25×10^{-3} cm/s). The reaction was substantially limited by the mass transfer of oxygen through the liquid aqueous film. At low liquid flow rates they likewise concluded that a portion of their catalyst was not wetted.

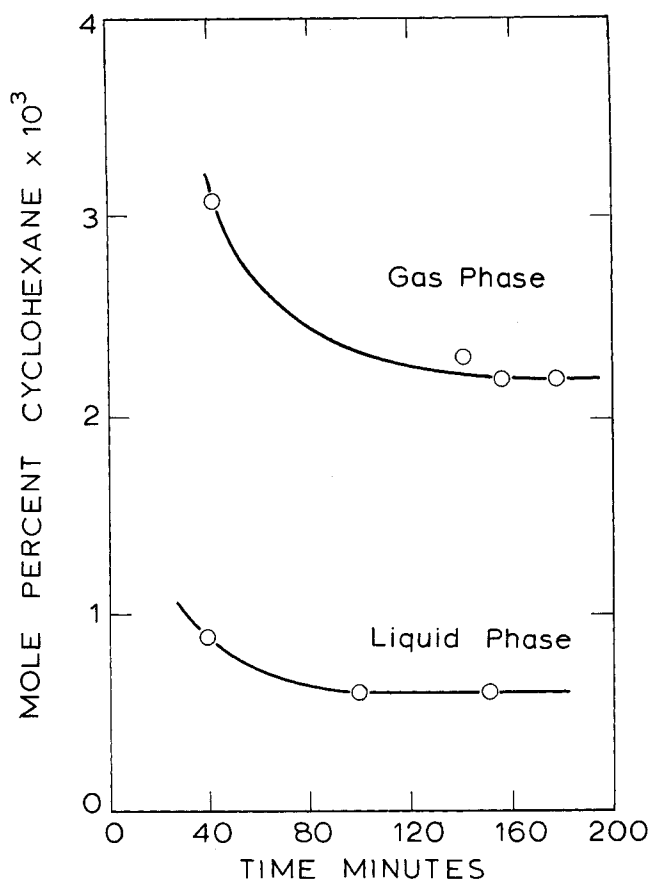


Fig. 1. Change in cyclohexane concentration in liquid and gas phases with time run no. 2.

SOME GENERAL COMMENTS

Even with excellent initial liquid distribution, the liquid in a trickle bed reactor may tend to flow downward in rivulets, but the degree of non-uniformity of liquid distribution will decrease as liquid flow rates are increased. Axial dispersion of the liquid in trickle beds is much greater than in single-phase flow because of such phenomena as stagnant liquid pockets and the mixing of liquid streams of different composition. The contribution to axial dispersion from diffusion in the catalyst pores may be different with rivulet-like flow than if all pellets are bathed in liquid since in the former case liquid may have to diffuse through one or more pellets to reach a rivulet, thus causing a greater effective path length for diffusion.

At low liquid flow rates the use of an average film thickness in a criterion for estimating mass transfer limitations through the trickling film may be an over-simplification if this resistance is major. Surprisingly little is known about external mass transfer under trickle bed conditions, and this is a weak link in analysis of trickle bed reactor performance. The fact that a relatively high liquid flow rate seems to be needed to ensure that all catalyst pellets in a trickle bed are covered with a liquid film may be of particular importance if an inert liquid is being used to minimize temperature effects or to wash off deposits or coke precursors or if a complex reaction is being catalyzed which has a different selectivity in the liquid and the gaseous phases.

Concurrent gas-liquid upflow operation is an alternative to trickle-bed processing and provides a means of ensuring that all catalyst pellets are directly contacted with liquid. However, mass transfer limitations in catalyst pores

are more likely to occur if they are filled with a liquid than with a vapor, thus a partially-wetted trickle bed may exhibit a higher reaction rate than a completely wetted one or an upflow reactor. Another factor to consider in comparing the two means of contacting is the volatility of the reactant. With a relatively volatile reactant, a partially-wetted trickle bed may show a greater rate of reaction than an upflow flooded bed reactor while the reverse is more likely with a reactant predominantly in the liquid phase, if diffusion limitations occur.

The above comments assume that the rate of a simple reaction will be the same in the liquid and gaseous phases when the two are nearly in equilibrium and mass transfer limitations and adsorption effects are absent. This was shown indeed to be the case in a recent study of the isomerization of cyclopropane on a silica-alumina catalyst in the presence of an inert liquid in a trickle bed reactor (Satterfield and Way, 1972).^{*} In that study, in which values of L varied from 0.068 to 0.27 cm/s, the consistency of the data on Arrhenius plots, the close agreement of the apparent activation energy both internally and with literature values, the excellent reproducibility of liquid holdup experiments and the quick establishment of a new equilibrium holdup upon changing flow rate all indicate that partial wetting of the catalyst did not occur. Mass transfer limitations through the trickling film were small in almost all cases so that an irregular flow pattern of the liquid would presumably have had little effect on the results. Judging from the criterion of Mears (1971) axial dispersion likewise was an insignificant effect in that study.

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NOTATION

- L = superficial liquid velocity, cm/s
- μ = viscosity, poise = g/(s) (cm)
- d_p = catalyst particle diameter, cm
- γ = ratio of hydrogen concentration at liquid-solid interface to that at gas-liquid interface
- ρ = liquid density, g/cm³

LITERATURE CITED

- Hartman, M., and R. W. Coughlin, "Oxidation of SO₂ in a Trickle Bed Reactor Packed with Carbon," *Chem. Eng. Sci.*, **27**, 867 (1972).
- Mears, D. E., "The Role of Axial Dispersion in Trickle-Flow Laboratory Reactors," *ibid.*, **26**, 1361 (1971).
- Özel, Fahri, "The Performance of Trickle Bed Reactors," S.M. thesis, Massachusetts Inst. of Technol., Cambridge (1973).
- Petrovic, L. J., and G. Thodos, "Mass Transfer in the Flow of Gases Through Packed Beds. Low Reynolds Number Region," *Ind. Eng. Chem. Fundamentals*, **7**, 274 (1968).
- Satterfield, C. N., and P. F. Way, "The Role of the Liquid Phase in the Performance of a Trickle Bed Reactor," *AIChE J.*, **18**, 305 (1972).
- Sedricks, W., Ph.D. thesis, "Three-Phase Reactors," Univ. of Cambridge, England (1969).
- , and C. N. Kenney, "Partial Wetting in Trickle Bed Reactors—the Reduction of Crotonaldehyde over a Palladium Catalyst," *Chem. Eng. Sci.*, **28**, 559 (1973).

^{*} In the first paragraph on page 310 of this reference, the symbols η and γ were transposed. The smallest value of γ observed, at 111°C, was 0.75.

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