A Hollow-Fiber Trickle-Bed Reactor

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Hollow fibers can be effective as trickle-bed reactors, and offer advantages over conventional trickle beds under special conditions. In this note we present research that partially identifies these conditions.

Trickle-bed reactors are widely employed to carry out multiphase catalytic chemical reactions. In such a reactor, a liquid reagent flows downward through a catalyst bed, while gaseous reactants flow either upward or downward through the bed. The gaseous reactants dissolve into the liquid medium, diffuse to the surface of the catalyst particles, and then react. The products dissolve in the liquid.

The flow rates in such a reactor can be restricted by channeling, incomplete loading, or flooding. One way to reduce these restrictions is to introduce hollow fibers to the catalyst bed, so that the gas and liquid flow independently. Such independent flows sustain the large interfacial area over a wide range of conditions. The question is the effect of these hollow fibers on the reaction rate.

Analysis

To focus our discussion, we consider the case of a first-order, irreversible chemical reaction. The rate of this reaction in a hollow-fiber trickle-bed reactor is given by

$$N_1 = K\underline{a}Vc_1 \tag{1}$$

where N_1 is the molar flux; K is an overall mass transfer coefficient; $\underline{a}$ is the fiber area per reactor volume; V is the total volume of the reactor; and c_1 is the gas concentration of the reagent. This gas concentration is the same in hollow-fiber and conventional trickle beds. The surface area per volume in a hollow-fiber reactor is usually larger than that in a conventional two-phase reactor: values of $\underline{a}$ in hollow-fiber modules are often 10 cm^2/cm^3 (300 ft^2/ft^3), and values more than ten times as large are quoted (Matson et. al., 1983).

The reaction rate in this type of reactor is governed by the overall resistance to the reaction $(1/K\underline{a})$

$$\frac{1}{K\underline{a}} = \frac{1}{k_{gas}\underline{a}} + \frac{1}{k_{mem}\underline{a}} + \frac{m}{k_{liq}\,\underline{a}} + \frac{m}{k_{cat}\underline{a}'} \tag{2}$$

where each of the terms $(1/k_i\underline{a})$ corresponds to a different resistance, and $\underline{a}'$ is the catalyst area per reactor volume. That in the gas $(1/k_{gas}\underline{a})$ is usually small because diffusion in the gas is fast (Cussler, 1984). That in the membrane $(1/k_{mem}\underline{a})$ is also small if the membrane is porous and not wetted by the surrounding liquid (Yang and Cussler, 1986; D'Elia et al., 1986).

The remaining two resistances, which represent that in the liquid and that of the catalyst particles, are commonly larger than the first two terms, and hence determine the overall rate of reaction. Both resistances are increased by the partition constant m, the ratio at equilibrium of the reagent concentration in the gas divided by that in the liquid. The value of k_{liq} is often around 10^{-3} cm/s, reflecting the narrow range of diffusion coefficients in liquids. The value of k_{cat} varies widely, because it includes both mass transfer from the bulk liquid to the catalyst surface and diffusion and reaction within the porous catalyst.

Both $k_{liq}\underline{a}$ and $k_{cat}\underline{a}'$ are independent of the gas flow rate. Obviously, $k_{liq}\underline{a}$ will vary with the area per volume of hollow fibers, but $k_{cat}\underline{a}'$ will not. Less obviously, both $k_{liq}\underline{a}$ and $k_{cat}\underline{a}'$ will vary with the liquid flow. The latter does so because it includes mass transfer at the catalyst surface.

Experiments

To put these ideas on a more specific basis, we report experiments on the room-temperature oxidation of SO_2

$$SO_2 + \frac{1}{2}O_2 + H_2O \xrightarrow{\text{activated carbon}} H_2SO_4 \tag{3}$$

Because O_2 is much less soluble than SO_2 in water, O_2 is the limiting species in this reaction.

The reactor, shown in Figure 1, is made of a hollow-fiber module with activated carbon in its shell side (Matson et al, 1983). This module has 61 fibers (Celgard X20, Questar) of 0.0413 cm ID, potted with HB Fuller FE-5045 epoxy resin in a Pyrex column of 1 cm ID. The catalyst is activated carbon (Norit, North American Carbon) with a particle size of 35 × 100 mesh, or an average particle diameter of 0.032 cm. The aqueous solution in the reservoir is circulated through the shell

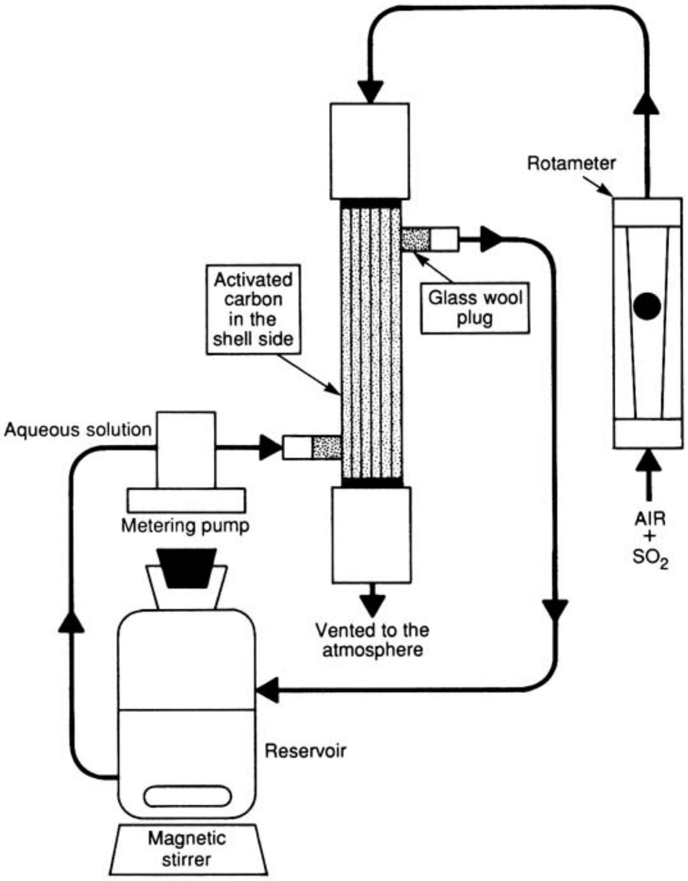

Figure 1. Apparatus for hollow-fiber experiments.

The hollow fibers allow gas and liquid flows to be adjusted independently. Being microporous and hydrophobic, the fibers offer no resistance to mass transfer.

side of the reactor, while a mixture of air and SO_2 is blown through the tube side. The aqueous concentration of dissolved O_2 is determined by an oxygen electrode (97-08-00, Orion Research). The concentration of SO_3^{2-} is determined by the iodimetric method: a sample is mixed with excess 0.05N I_2 and back-titrated with 0.025N $Na_2S_2O_3$ using starch as the indicator. The concentration of SO_4^{2-} is determined by mixing a sample with hydrogen peroxide, which oxidizes all the unreacted SO_3^{2-}, followed by titrating with 0.01N NaOH to pH 7 using Hydrion Vivid indicator (Kolthoff and Sandell, 1952). By subtracting the concentration of SO_3^{2-} from the result of acid titration, the true concentration of SO_4^{2-} can be found. The reaction rate is calculated from

$$N_1 = Wr = V_R \frac{d(SO_4^{2-})}{dt} \qquad (4)$$

where r is the reaction rate in mol/g cat · s, W is the mass of the catalyst, and V_R is the total volume of the reservoir.

The results found with this hollow-fiber reactor are compared in Figure 2 with those found using a conventional trickle-bed reactor (Berruti et. al., 1984). The results show interesting features at low liquid flow, and at high liquid flow. At low liquid flow, our results are consistent with those found previously. Both systems show that the reaction rate increases as the flow increases. We believe that this is because the mass transfer in the liquid is accelerated by faster flow. At intermediate flow, our reaction rates are faster than those found previously. These increases occur at liquid velocities that cause flooding in a conventional liquid bed. At high flow, our reaction rates seem to approach an asymptote. We suspect that this asymptote represents a reaction independent of mass transfer and controlled by chemical kinetics.

Thus the hollow-fiber trickle-bed reactor gives faster reaction

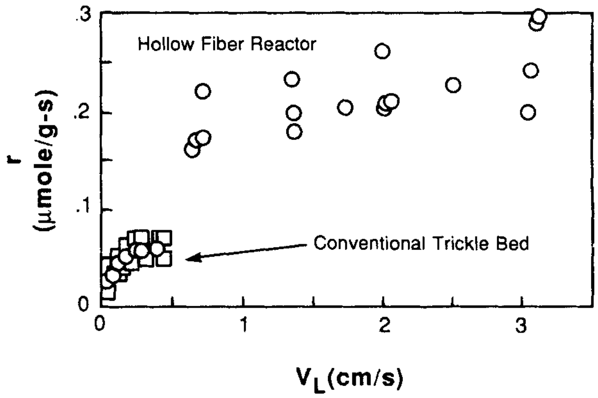

Figure 2. Sulfur dioxide oxidation with hollow fibers.

The results at low flow are the same as in a conventional trickle bed, but are faster at high flow. Our data, O; conventional data, □.

rates than the conventional trickle-bed reactor. We expect such fibers to give superior results whenever mass transfer influences the kinetics.

Acknowledgment

This work was largely supported by the Celanese Corporation. Other support came from the National Science Foundation, Grant Nos. CPE 8408999 and CBT 8611646.

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Manuscript received Jan. 14, 1987, and revision received Mar. 19, 1987.