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Department of Chemical Engineering   **Joseph J. Martin**
The University of Michigan
Ann Arbor, Michigan 48109

Experience with an All-Glass Internal Recycle Reactor

Sir: We would like to clarify several issues raised in the recent correspondence of Berty (1979) and the article by Fitzharris and Katzer (1978). We find that an all-glass internal recycle reactor has limited but very useful application in kinetic and poisoning studies of real catalysts—particularly monolithic catalysts.

Our quartz internal recycle reactor is of the same design as that described by Fitzharris and Katzer (1978). We confirmed ideal-mixing behavior of the reactor by transient response tests. We were also able to reproduce methanation turnover numbers and activation energies on supported nickel in pellet, powder, and monolithic form within 20–25% of those obtained in tubular reactors and within a factor of 2 compared to data from the literature (see Table I).

Berty criticized the all-glass reactor, commenting that at low pressure the glass impeller may not develop sufficient pressure head to cause significant flow through a bed of catalyst particles. Based on pressure drop calculation, he predicted a flow through a single particle diameter deep bed in the glass reactor of about 0.2 m s^{-1} (at 1 atm and 1000 rpm), approximately one-sixth the flow needed to produce incipient turbulence.

We checked this experimentally by means of a hot-wire anemometer measuring air flows developed by the stirring unit at ambient pressure (86 kPa) through monolithic and particulate catalysts. We also calculated flows using Berty's equations for comparison with our experimental measurements of air flows. Table II shows the calculated and measured flows.

In the case of the particulate catalysts, the measured flows are a factor of 10 less than calculated values. We believe the lower than expected flow can be attributed to a thin layer of quartz wool used to support the particulate samples. Comparison of the measured flow with the outlet flow indicates a recirculation ratio of unity for the particulates. However, for the monolithic catalyst the measured flow is only a factor of 3 lower than the calculated value; this is anticipated since the length of the bed exceeds the monolithic channel diameter by about a factor of 3. Moreover, the observed recirculation ratio is 15 for the monolith. Thus a reasonable flow with considerable recycle can be developed through the monolith but not through the particulate samples. In actual operation, higher flows and recirculation ratios would be possible since the reactor can be pressurized to obtain at least a factor of 2 increase in pressure with a proportional increase in pressure head. Moreover, the depth of the monolithic bed could be decreased by at least a factor of 2–3. In other words, it is possible to obtain flows of 0.5–0.6 m s^{-1} through a monolithic catalyst bed in the all-glass reactor.

Berty suggested that a velocity greater than 1.4 m s^{-1} is desirable to obtain turbulent flow in a catalyst bed. The implication is that turbulent flow is needed to avoid nonideal flow patterns which adversely affect the measurement of reaction rates. However, our experimental results in Table I suggest that this is not a serious problem for our thin beds and particular reaction conditions.

Table I

catalyst	turnover no. $\times 10^3$ [c]
All-Glass Internal Recycle Reactor	
6% Ni on Al$_2$O$_3$ powder	3.2
6% Ni on Al$_2$O$_3$ pellets	3.1
3% Ni on Al$_2$O$_3$ monolith	2.2
Tubular Fixed-Bed Reactors	
6% Ni on Al$_2$O$_3$ spheres[a]	2.5
5% Ni on Al$_2$O$_3$ powder[b]	1.0

[a] Jarvi, G. A., Mayo, K. B., Bartholomew, C. H., to be published in *Chem. Eng. Commun.*, 1979. [b] Vannice, M. A., *J. Catal.*, 37, 449 (1975). Calculated using his rate expression and activation energy. [c] In molecules of CH$_4$ produced/site-s (at 500 K, 1 atm).

Table II

catalyst	calcd flow[a] of air, m/s	measd flow of air, m/s	recirc ratio
40 mesh Al$_2$O$_3$[b]	0.20	0.02	1
0.32 cm diameter Al$_2$O$_3$ pellets	0.20	0.02	1
cordierite monolith 31 □/cm^2 [d]	0.33[c]	0.10	15

[a] Using the equation of Berty (1979) and 1000 rpm. [b] Supported on a 1–2 mm layer of quartz wool. [c] Using the pressure drop expressions of Hegedus, presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1973. [d] 1 cm long × 2.5 cm diameter.

Presumably if laminar flow patterns were affecting the rate measurements, a change in flow direction through the reactor (particularly of the Fitzharris–Katzer design) would reveal this; however, upon reversing the inlet and outlet streams, the rates and conversions were found to be the same (within ±3–5%). Perhaps in thin catalyst beds, entrance effects and developing laminar flow serve to produce plug-flow-like patterns.

Thus our experience confirms Berty's opinion that the all-glass recycle reactor is limited primarily to the study of films and thin catalyst beds at low pressure. Nevertheless, we think it has broader application than he implied. It is in our opinion a convenient, low-cost tool for obtaining accurate kinetic and poisoning data of practical as well as theoretical value for almost any real catalyst, because in principle any solid catalyst can be prepared in monolithic form (Deluca and Campbell, 1977). In addition, the quartz reactor enables sulfur poisoning studies to be conducted at low but industrially relevant poison concentrations (e.g., 0.001 to 1 ppm of H$_2$S) where essentially all practical metal systems and even Pyrex introduce serious adsorption and/or contamination problems (Fitzharris and Katzer, 1979; Bartholomew, 1979). We feel that this development by Fitzharris and Katzer of a reactor system inert to contamination by sulfur at such low concentrations is a remarkable contribution.

Finally, our experience recommends monoliths as the only practical catalyst form for use in the all-glass internal recycle reactor. Moreover, the use of monolithic catalysts provides an additional important advantage over particulate forms in kinetic studies—namely significantly lower pore diffusional resistance enabling intrinsic rates to be measured over a wide range of temperature and pressure using either glass and metal tubular reactors (Jarvi et al., 1979) or glass and metal internal recycle reactors (Bartholomew, 1979).

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Department of Chemical   **Calvin H. Bartholomew***
Engineering   **Erek J. Erekson**
Brigham Young University
Provo, Utah 84602

Experience with an All-Glass Internal Recycle Reactor

Sir: We appreciate very much the comments by Bartholomew and Erekson (1980). Their results fully support our observations (Fitzharris and Katzer, 1978) and quantify the behavior better than we had done. We saw no need to respond to the correspondence of Berty (1979) because we agreed with his comments. Our design and operation was never intended for catalyst beds of any significant depth.

We have used the reactor with flat plates (standing vertically in the reactor) of α-Al$_2$O$_3$ having metal (Fe, Ni, Co, and Ru) evaporated or impregnated on their exterior surface, with open 4-cm cylinders of quartz and α-Al$_2$O$_3$ having metal evaporated or impregnated on their exterior surfaces, with commercial catalyst pellets, and with pellets having the metal deposited on a very thin peripheral region near the exterior particle surface. The pellets, plates, and cylinders were supported on a quartz grid, and we have used typically one to four pellets, which we would consider a shallow bed since it has more than 60% open space for gas flow.

In mixing studies using smoke with these catalyst configurations we have qualitatively estimated gas flow velocities of about 0.5 m/s. We have also, as Bartholomew and Erekson (1980) have reported, observed turnover numbers within a factor of 2 of those reported in the literature for CO hydrogenation and activation energies that were identical with those reported in the literature for Ni,

Co, Ru, and Fe. Obviously mass and/or heat transfer problems were not important for our catalyst configurations. We would agree with Berty (1979) and Bartholomew and Erekson (1980) that deeper catalyst beds would cause problems.

The major advantage of the reactor in the quartz version is that quantitative catalyst poisoning studies can be carried out at H$_2$S levels as low as 10 ppb and probably lower without contamination from the reactor (Fitzharris, 1978; Agrawal, 1979). We have clearly shown that Pyrex cannot be used for such low sulfur concentrations because of reactor contamination and most metal reactors would be expected to give contamination problems which are at least as serious.

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Center for Catalytic Science and   **William D. Fitzharris**
Technology   **James R. Katzer***
Department of Chemical
Engineering
University of Delaware
Newark, Delaware 19711