COMMUNICATIONS TO THE EDITOR

Tubular Reactors: Effect of Flow Profile on Conversion for a Nonelementary Reaction

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Conversion for homogeneous reactions occurring in tubular reactors is dependent on the flow regime. Although design equations for these reactors based on the assumption of plug flow are well established, how to handle laminar flow conditions has been a subject of continuing research (*1*, *4* to *7*, *11*). Typical of one approach is that presented by Rothenberg and Smith (*9*, *10*), where the equations of change are solved numerically to give radial profiles of concentration and temperature. These profiles are integrated to yield bulk composition or temperature as a function of axial position. Such a procedure was used by Merrill and Hamrin (*7*) for the industrially important demethylation of toluene to benzene. They found for a specific set of isothermal operating conditions that a 12% loss in conversion is suffered in going from turbulent to laminar flow. In this communication, we present a generalized method of comparing laminar and plug-flow reactors for irreversible, nonelementary reactions of the type

$$A + B \rightarrow \text{Products}$$

occurring under isothermal, constant density conditions.

The demethylation of toluene is an example of such a reaction since its rate expression is given by

$$\frac{d\xi}{dt} = k(a_0 - \xi)(\gamma a_0 - \xi)^{1/2} \tag{1}$$

where ξ is the extent of reaction (*2*), a_0 is the inlet toluene concentration, and γ is the inlet hydrogen/toluene ratio.

Integrating Equation (1) gives the extent of reaction as a function of residence time for a plug-flow reactor (PFR)

$$x = \frac{\xi(t)}{a_0} = \gamma - (\gamma - 1)\left(\frac{1 + Ce^{\kappa}}{1 - Ce^{\kappa}}\right)^2, \quad \gamma > 1 \tag{2}$$

where

$$C = 2\left[\gamma + \sqrt{\gamma(\gamma - 1)}\right] - 1$$

$$\kappa = \sqrt{a_0(\gamma - 1)}\,kt$$

For completely segregated flow the mean extent is given by

$$\bar{\xi} = \int_0^{\infty} p(t)\xi(t)dt \tag{3}$$

and for a laminar-flow reactor (LFR) the residence time distribution (RTD) is given by Aris (*2*)

$$p(t) = \begin{cases} 0 & 0 \leq t < \theta/2 \\ \theta^2/2t^3 & \theta/2 < t \end{cases} \tag{4}$$

Substituting Equations (2) and (4) into Equation (3) yields

$$\bar{x} = \frac{\bar{\xi}}{a_0} = \int_{1/2}^{\infty}\left[\gamma - (\gamma - 1)\left(\frac{1 + Ce^{\bar{\kappa}\tau}}{1 - Ce^{\bar{\kappa}\tau}}\right)^2\right]\frac{d\tau}{2\tau^3} \tag{5}$$

where $\tau = t/\theta$ and $\bar{\kappa} = \kappa/\tau$. We were unable to integrate this expression analytically so a Gaussian quadrature technique was used to evaluate numerically the integral on an IBM 360/65 computer. Values of $\bar{x}$ as a function of $\bar{\kappa}$ were obtained over the range of $0.01 \leq \bar{\kappa} \leq 10$ at $\gamma = 1.01$, 2, 5, and 100. Next x was computed from Equation (2) for $\kappa = \bar{\kappa}$, that is, equal residence times. The results are plotted as the dimensionless ratio of extent in laminar flow to extent in plug flow

$$X = \frac{\bar{\xi}}{\xi} = \frac{\bar{x}}{x} \tag{6}$$

against the dimensionless time, $\bar{\kappa}$ in Figure 1. For nearly equal concentrations of the two reactants ($\gamma = 1.01$), $X_{\text{min}} = 0.891$ which occurs at $\bar{\kappa} = 0.07$. The magnitude of X_{min} is quite insensitive to variations in γ with the least value ($X_{\text{min}} = 0.881$) occurring at $\gamma = 100$. The dimensionless time, however, at which X_{min} occurs varies over a considerable range from 0.07 to 0.9. It is apparent that laminar flow gives less conversion for a given dimensionless time except at very high conversions where the difference is negligible.

For large γ the term $(\gamma a_0 - \xi)^{1/2}$ in Equation (1) can be considered constant; that is, under these conditions rate behavior is pseudo-first order. In the scale of Figure 1 no

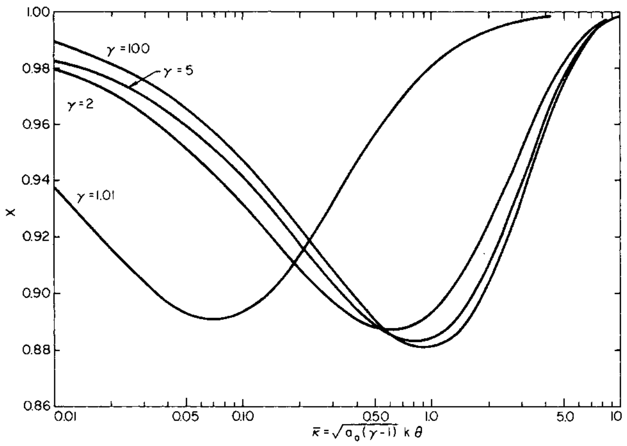

Fig. 1. Ratio of the conversion with a laminar flow profile to that with plug flow for various reactant ratios.

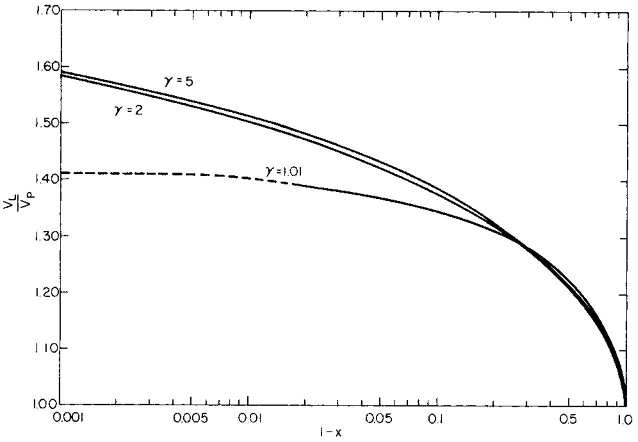

Fig. 2. Ratio of laminar to plug flow reactor volume required for a given conversion.

difference could be determined between the $\gamma = 100$ and the first order results given by Aris (2) over the range $0.9 \leq \bar{\kappa} \leq 8$.

An alternate method of comparing laminar and plug flow reactors was given by Denbigh (3) for a second-order reaction. He presented a tabulation of LFR volume/PFR volume required for the same conversion

$$\frac{V_L}{V_P} = f(x, X = 1) \qquad (7)$$

Novosad and Ulbrecht (8) applied this method to various order reactions for both Newtonian and power-law fluid RTD's.

For the 1.5 order reaction under consideration, this ratio was obtained from a numerical integration of Equation (5) which gave values of $\bar{x}$ at $\bar{\kappa}$ increments of 0.01. Equation (2) was solved for κ at values of $x = \bar{x}$ (equal conversions) generated by Equation (5). In this way

$$\bar{\kappa}/\kappa = \theta/t = V_L/V_P \qquad (8)$$

for equal initial concentrations and equal flow rates in the two types of reactors. The results are plotted in Figure 2 as V_L/V_P versus log $(1 - x)$ at $\gamma = 1.01$, 2, and 5. It can be seen that the volume required for a laminar flow reactor becomes significantly greater as conversion increases. At 99% conversion V_L is 40.5 to 51.5% greater than V_P as γ varies from 1.01 to 100. The increase in volume is most sensitive to a change in reactant ratio when the reactant concentrations are nearly equal. A curve for $\gamma =$ 100 is not shown because it is within 0.2% of the $\gamma = 5$ curve. As stated earlier, the results from $\gamma = 100$ can be considered pseudo-first order and are in agreement with previously published first-order calculations (8). As $\gamma \rightarrow 1$, Equation (1) becomes a stoichiometric, 1.5 order, rate expression which was treated earlier (8). Again the $\gamma = 1.01$ results are in good agreement.

Finally the curve for $\gamma = 5.0$ extends the results of Merrill and Hamrin (7, Figure 4) shown for isothermal LFR and PFR's over a much greater range of conversion.

In summary, we have presented a general method for comparing laminar and plug-flow reactors, which illustrates the conversion loss suffered for a given reactor or the reactor volume increase required for a given conversion under laminar flow conditions. In addition, the importance of changes in the inlet reactant ratio was determined for the first time in applying the method to a 1.5 order reaction.

NOTATION

A = limiting reactant
a_0 = inlet concentration of A
B = reactant in excess
C = constant in Equation (2)
k = reaction rate constant
$p(t)$ = laminar flow RTD defined by Equation (4)
t = residence time of each element in reactor
V_L = volume required for a specified conversion in LFR
V_P = volume required for a specified conversion in PFR
x = conversion of A in PFR
$\bar{x}$ = conversion of A in LFR
X = dimensionless ratio of extent (or conversion)
$X_{\min}$ = minimum value of X

Greek Letters

γ = inlet reactant concentration ratio
θ = average residence time
κ = dimensionless residence time in PFR
$\bar{\kappa}$ = dimensionless residence time in LFR
ξ = extent of reaction in PFR
$\bar{\xi}$ = extent of reaction in LFR
τ = dimensionless residence time of each element in reactor

LITERATURE CITED

1. Andersen, T. S., and J. Coull, *AIChE J.*, **16**, 542 (1970).
2. Aris, R., "Elementary Chemical Reactor Analysis," Prentice-Hall, Englewood Cliffs, N. J. (1969).
3. Denbigh, K. G., "Chemical Reactor Theory," Cambridge University Press, Cambridge (1965).
4. Homsy, R. V., and R. D. Strohman, *AIChE J.*, **17**, 215 (1971).
5. Johnson, M. M., *Ind. Eng. Chem. Fundamentals*, **9**, 681 (1970).
6. Koo, L., and E. N. Ziegler, *Chem. Eng. Sci.*, **24**, 217 (1969).
7. Merrill, L. S., Jr., and C. E. Hamrin, Jr., *AIChE J.*, **16**, 194 (1970).
8. Novosad, Z., and J. Ulbrecht, *Chem. Eng. Sci.*, **21**, 405 (1966).
9. Rothenberg, R. I. and J. M. Smith, *AIChE J.*, **12**, 213 (1966).
10. *Ibid.*, *Can. J. Chem. Eng.*, **44**, 67 (1966).
11. Wan, C., and E. N. Ziegler, *Chem. Eng. Sci.*, **25**, 723 (1970).